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AN INTRODUCTION TO CRYSTAL ANALYSIS

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BY
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PREFACE

This book is founded on a course of lectures which was given at the University College, Aberystwyth, in the autumn of 1926. The lectures were intended for a general audience ; and consisted, accordingly, of a series of simple illustrations of the main features of crystal analysis. It would not have been possible to do more within the limits imposed by time and the circumstances. The treatment in this book is somewhat fuller and more varied than that of the lectures.

I hope that the book may be of service to those who wish to understand the main principles of the new subject. Since V. Laue suggested the first experiments, and my son, W. Lawrence Bragg, showed that a new method of crystal analysis was now available, astonishing progress has been made. A record of the work done becomes a treatise, and a very technical treatise at that. I find that many of my friends, preoccupied with their own work, have been obliged to give up reading the stream of papers conveying accounts of new research. At the same time, it is more clear than ever, and I think the fact is generally recognised, that the crystalline state of materials is of importance to a great number of the sciences. I have, therefore, tried to make clear the phraseology of the subject, both that which had already been adopted by the older crystallography and that which is now required by the introduction of the X-ray methods. I have also set out the main principles and the methods founded upon them ; and have proceeded to a certain number of examples of analysis. These will be found sufficient, I hope, to illustrate the powers of the subject, to give some idea of the direction in which it is advancing, and to make it possible to forecast future applications.

I have inserted only a few references, as I did not wish to interrupt the continuity of the narrative : full references are to be found in any of the treatises already written. It is all the more necessary for me to acknowledge that the material of the book is drawn from many sources, especially from the work of my son and his colleagues at Manchester, and from the researches of my own colleagues in the Davy Faraday Laboratory. I am grateful to the Royal Society, to the Chemical Society, to the Institution of Mechanical Engineers, to the British Association for the Advancement of Science, and to the proprietors of *Nature* for their permission to reproduce various illustrations. I have also to thank Dr. Clark, lately of the Massachusetts Institute of Technology, for permission to publish a few examples of his applications of the X-ray methods to industrial purposes.

Finally, it is an especial pleasure to have an opportunity of thanking my friends at Aberystwyth for their kindness and courtesy on the occasion when the lectures were given.

W. H. BRAGG.

The Royal Institution of Great Britain,
June, 1928.

CONTENTS

CHAPTER		PAGE
I.	Reflection by the Crystal Lattice	1
II.	Methods of Analysis	27
III.	Simple Inorganic Crystals	56
IV.	Space Groups or Crystal Arrangements	89
V.	Some Complex Crystals	113
VI.	Metals	143
	Appendix	163
	Index	167

CHAPTER I

REFLECTION BY THE CRYSTAL LATTICE

In 1912 M. Laue suggested the trial of an experiment which if it were successful would prove that Rontgen rays, as to the nature of which there had been protracted arguments, were of the same nature as the rays of light : there might be, there certainly would be, a difference in quality, but not in kind. The experiment was made by Friedrich and Knipping in the laboratory of the University at Munich. A fine pencil of Rontgen rays was passed through a crystal and allowed to fall upon a photographic plate. After an exposure of many hours the plate was developed, and there appeared a symmetrical arrangement of spots centred about an intense over-exposed spot which was due to the action of the direct pencil. Two modern examples of these 'Laue' photographs are shown in Figs. 1 and 2, Plate I. They are due respectively to Dr. W. M. Lehmann and to Dr. A. Müller (see later p. 133). In the first figure the crystal used is beryl, a crystal of high symmetry based on a hexagonal structure ; in the second stearic acid, a crystal of low symmetry. We shall come presently to the explanation of the appearance of the photographs. Laue had anticipated some such result. The experiment furnished a convincing proof that the X-rays were of the same nature as light ; and was a complete and most striking success.

The reasons that prompted Laue to try this experiment are of great interest, in view of what we have before us in these lectures. He had in his mind the optical effect known as diffraction, which in one form or another is of common occurrence. The halo round the moon or round any bright source of light when viewed through a fog, or through a sheet of glass dimmed with moisture, the star rays or asterisms that radiate from a bright point seen through a

fine woven material, the play of colour on mother of pearl, the colours of the peacock's feather and the butterfly's wing are all of them examples of diffraction. For their production certain conditions must be satisfied. There must be a regularity in the wave motion of the light, and there must be a regularity in the diffracting material; also the two regularities must be of approximately the same linear dimensions. The even spacing of the waves in the light train supplies the first requisite. The second may be the evenness of size of the particles in the atmosphere through which the moon's rays pass, or of the drops on the pane of glass, or it may be the rough regularity of the striations on the mother of pearl. Nature distributes over the feather or the wing of the butterfly, or the wing case of the beetle, a regular array of fine points which produces gorgeous and unfading colours. When she wishes her colour effects to be lasting she does not use dyes such as these on which the colours of flowers and leaves depend. The explanation of the diffraction effects in terms of wave motions in the ether was one of the triumphs of the nineteenth century workers, Young, Fresnel, Airy and others.

Laue imagined that some sort of diffraction effect might be observed when X-rays were substituted for light, provided that the requisite conditions were still fulfilled. As there was reason to suppose that the X-rays, if they were ether waves at all, would be some ten thousand times shorter than the waves of light, it was necessary to provide some regular arrangement correspondingly more minute than the arrangement or uniformity of particles which produced the diffraction effects of optics. He supposed that such an arrangement, regular, and of the right dimensions might be found in a crystal. Hence his experiment. Its success lay in the fact that it gave what was obviously a diffraction pattern, though of a novel kind. It linked up X-rays with light. It was a bold venture; but it is to be remembered that at the time of the experiment no other method of proving the identity in nature of light and X-rays had met with much success. There were no X-ray effects, for example, analogous

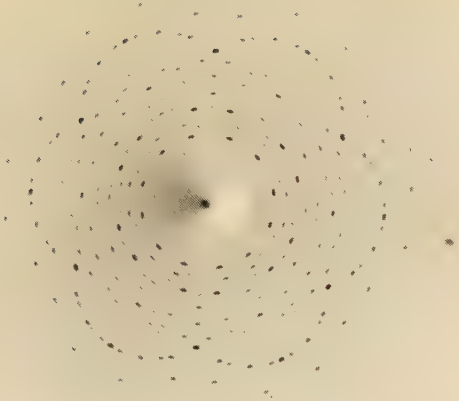

FIG. 1.—Beryl (Wm. Lehmann).

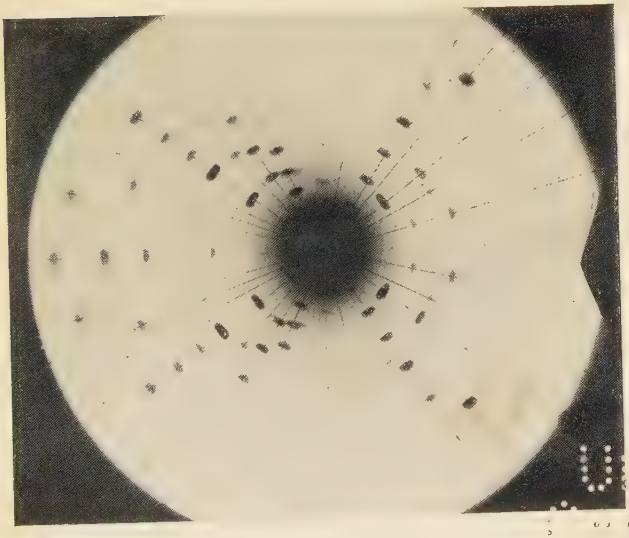

FIG. 2.—Stearic acid (Müller).

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to the reflection and refraction of rays of light, which effects are very familiar to us, and indeed provide the chief methods by which we recognise the action of light and the presence of objects.

Important as this demonstration was in its achievement of its original purpose, its unforeseen consequences have been even more striking. We now have, as we shall shortly see, nothing less than a method of examination of the structure of solid substances. Hitherto we have had no method at all: we have only been able to make a few suggestions based on indirect arguments from the facts of crystallography, from surface actions and the like. There is no necessity to describe the importance of such an addition to our means of studying nature. The properties of solid bodies affect us on every hand. The earth itself is solid, and carries on its surface living things, every one of which, plant or animal, is built round a solid structure: and not only are we ourselves solids but so also are our materials and our tools and the things we handle every day.

The physical properties of solid substances are to be referred not only to their composition in terms of atoms and molecules but also to the arrangement of these components and to the forces that bind them together. The circumstances of the solid, those essential features which give the solid its characteristics are not to be found in the liquid or the gas; the study of liquids and gases therefore contributes little to the further understanding which we desire. We have learnt something of the nature and the properties of atoms and molecules when more or less free from each other's influence; but we now enter upon quite a new realm of investigation, namely, the circumstances of their linking together into a rigid structure under the influence of ties of which we know very little.

To take a simple illustration, the properties of the molecules of oxygen and of hydrogen are well known to us in their independent existence as constituents of gases, and the properties of the combined molecule of water are studied in hydrodynamics; but the physical properties of ice and the

hexagonal form of the crystal are due to atomic and molecular actions of which little is known that is really definite. There is certainly a close connection between the properties and the structural arrangement of the atoms on the ice crystal, but as there has not been until now any way of discovering the latter, a whole field of enquiry has remained closed. Or again, the elements silicon and oxygen go to the making of quartz, which with ice were *the* crystals of the ancients. We know something of the chemical actions of silicon and oxygen, but nothing at all of the action of those forces, whether they overlap the forces of chemical combination or not, which bind the crystal together, give it its peculiar form, account for its strange optical activity, for the piezo-electric and the pyro-electric effects, and for all the remarkable high temperature transformations into various forms of tridymite and cristobalite. These are structural properties, and again no enquiry into their relation to structure is possible until the latter is discovered. And so it is with all other crystals, and also with crystalline aggregates and conglomerates into which classes so many substances fall : even with amorphous solids if such things really exist. The more we think of the matter the more far reaching do the new methods appear : the roads in the new country stretch away to the limits of vision.

Let us now consider how it is that Laue's experiment was more than a mere verification of a well-imagined hypothesis. How does it come to give us these new opportunities ?

We accept the evidence of Laue's experiment as proving the existence of a regular train of waves in the beam of X-rays, or at least that light and X-rays are alike. The regularity of structure of a crystal is also proved, if indeed it needed any further demonstration. Let us think what is implied by this latter regularity, which we have always imagined and are now to find so useful. Clearly, there is some inherent property of atoms and molecules which causes them to associate into very regular structures if the circumstances allow. When, for example, a solution of copper sulphate is evaporating and the molecules begin to

sort themselves out of the liquid and to associate in groups, in other words to crystallise out, the preciseness and constancy of the form which the grouping assumes tell us clearly that the solidification is not a mere gathering of the molecules into a jumble heap. The faces of any crystal of copper sulphate make the same angles with each other as the corresponding faces of any other crystal of copper sulphate. It is true that the circumstances of growth may affect the relative rates at which the faces grow, but this only means that more molecules have been added in certain directions than in others. We can draw from these facts no other deduction than this, that there is in the structure a unit of pattern containing copper, sulphur and oxygen atoms in the same proportions as that in which they occur in the molecule. Further, each unit must lie up against each neighbouring unit in precise fashion ; the relative orientation of the two and their relative distance apart being the same throughout the structure. The particular form of the crystal is a direct consequence of the particular structure of the unit. It is not possible, however, to deduce the latter from the former, or it would have been done long ago. But, now that the X-rays have come to our help, we obtain the power of looking past the outer appearance into the internal arrangement. The immense variety in the forms of various crystals, and the ease with which by precise measurements they can be distinguished from one another, are evidence of equal variety in the arrangement of the atoms and molecules in the unit and of equally precise distinctions. The structure of the single unit determine the properties of the solid substance. In many investigations of the behaviour of liquids and gases, in which the component molecules are not tied tightly together, the molecular form is of little consequence and it is sufficient to assume that it is spherical. But we cannot make this rough approximation when the molecules are associated into a solid crystal : for we should then blot out all those details which give each crystal its special characteristics. The chemical analysis of, for example, a piece of Iceland spar, calcium carbonate, begins

with its solution in the appropriate reagents. The ties that make the solid are broken at the outset, and all that is found from the analysis are the relative numbers of atoms of calcium carbon and oxygen. It is as if we knocked down a house and counted the number of bricks, planks, panes of glass and so on : in doing which we lose count of course of those associations which made the conglomeration into a house.

We must bear in mind also that there is something even more important than the solid itself, namely the boundary between solid and liquid or gas. It is here that a vast number of changes continuously take place which are essential to the processes of Nature, animate and inanimate. At the surface the free disorder of the liquid comes into contact with the solid and its constrained regularity. The two phases meet, interchange existences and exert mutual influences just as land and sea mutually encroach and affect each other. That is why the study of surface actions, of catalysis, and of colloidal phenomena are of such intense interest and importance. Now this surface action is greatly influenced by the orientation of the molecules of the solid ; one face of a crystal for example has not the same properties as another. We cannot expect to understand the behaviour of the surface unless we know what is at the back of it in the solid, and whether the regularity of the solid is continued to the surface absolutely or is modified as it approaches the open, and how the molecule presents itself to the liquid or gas outside, and what are the special properties of the portions so presented.

We have been making some use of the word molecule, which naturally stands for a certain combination of atoms known to us mainly from experiments with liquids and gases. As a matter of fact we have no right to do so ; for it does not follow that, because a certain number of atoms take up a special arrangement when their company is free and independent, they necessarily retain the same arrangement when built with others into a structure. Our only justification is that we can actually recognise the molecule in the crystal

in a very large number of cases. The recognition is not always clear, however, and we even find some cases in which there is such a regrouping of the atoms that a new molecule may be said to have been formed. There is always regularity in the arrangement within the crystal; but it is not strictly correct to say that it is an arrangement of the molecules unless the chemist will allow that his molecules can be altered: the change may be negligible in most cases but sometimes it is certainly considerable. If the alteration were so great that the chemical molecule was quite broken up and its atoms re-distributed, then our new field of enquiry would not be less in any way than we now find it, because it would still include all the connections between the properties of the solid and the atoms of which the solid is built; but we should lose a most interesting and useful connection with the great results of chemistry. We may consider ourselves fortunate because the connection is actually a strong one.

If it is not necessarily an arrangement of molecules, then, we must ask, what is it that is arranged?

We recognise at once that there must be some unit of pattern in the crystal: there must be an innumerable number of points such that if an observer, capable of taking up a position within the crystal and of noting the details of his surroundings, could be translated from any one of these points to any other, he would find no change in the outlook in any given direction in space. This supposes, of course, that the crystal extends to an infinite distance in all directions; but once the crystal is defined in this way we can suppose a finite crystal to be carved out of the infinite and to retain at the same time its structure, except perhaps in the neighbourhood of the surface. This is the fundamental characteristic of the crystalline arrangement; that which is in the first line responsible for the observed X-ray effects—we shall presently see how—and which is always the first object of measurement. We can conveniently represent it by the diagram of Fig. 3 in which each intersection of the dotted parallels, drawn in three directions in space, is one of the points mentioned above. The lines of the diagram are

not necessary to its usefulness : we might have used rows of points only. But they serve to make the construction clearer to the eye ; and they serve a second purpose in showing that space can be divided into cells, all exactly alike, the eight corners of each cell coinciding with eight of the points mentioned above.

The arrangement of points is known as a ' space lattice ' and the cell as the ' unit cell ' of the crystal, or the crystal

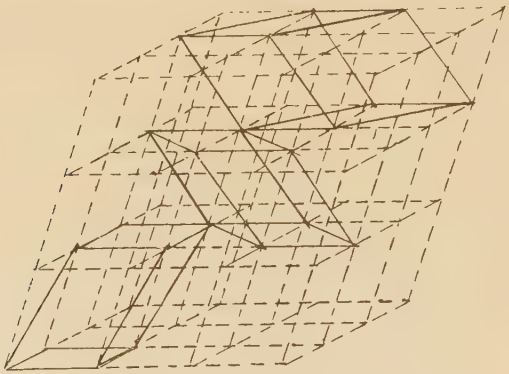


FIG. 3.—Space lattice and unit cells.

unit. Any point can be chosen to represent the unit of pattern provided all other units are represented by points similarly chosen. The whole point lattice, in other words, can be translated to any new position provided that the orientation with respect to the crystal is unaltered.

Retaining the same lattice of points, the cell can be drawn in an infinite number of ways. The dotted lines show one way : others are shown by the full lines of the diagram. The unit cell has necessarily the same volume whatever its shape.

There are as many points as there are cells. Each cell has eight corners, and at each corner is one of the points, which may be said to belong equally to eight cells and to give one-eighth of itself to each of them.

This main arrangement or space-lattice is all that we consider for the moment. Presently we shall find that within the cell is an extremely interesting inner arrangement which

can also be determined in nearly all cases. The cell contains the substance of one or more molecules, or, to speak more cautiously, similar groups of atoms, and the internal structure of which we speak is concerned with the disposition of these groups. A further stage, and the last, in the analysis of a crystal is the determination of the positions of the atoms in the group.

Confining our considerations for the time being to the main arrangement, or, what is the same thing, to the form of the unit cell, we have to observe that the number of molecules grouped about the point, or comprised within the cell—these two expressions are equivalent to each other—is usually small. It is one of Nature's facts that this is so : and it does not seem easy to give an explanation of it beyond saying that it must depend on atomic properties. In the case of rocksalt there is in each cell one molecule, consisting of one atom of sodium and one of chlorine. The aluminium cell contains one atom of aluminium. The diamond cell contains two atoms of carbon, and quartz the substance of three molecules of silicon dioxide. The unit cell of fumaric acid contains the substance of six molecules ; and in some cases, *e.g.* that of certain metal alloys, the number is greater still. But large numbers appear to be exceptional. The consequence is that the unit cell has an average size which happens to be most convenient for the application of the new method of analysis. The distance between any lattice point and its nearest neighbours is usually in single numbers of Angstrom Units, though occasionally values as high as fifty units are met with. The existence of the lattice and its usual size taken in conjunction with the length of the X-ray wave are the circumstances on which the success of the method depends.

We have said that the X-rays must be considered as wave-trains in the ether, differing only from light in that the length of the wave is to be measured in fractions of an Angstrom Unit instead of in thousands of such units. The range of X-ray wave-lengths usually employed is from about two Angstrom Units down to one-eighth of one unit. The wave-length of the *D* line of sodium is 5895·93 units. This

divergency must be held accountable for the great difference in the properties of the X-rays and light. Unlike the latter the X-rays are not turned back by the surface action of a mirror but penetrate all substances to a depth depending both on the wave-length of the ray and the composition of the substance : their singular properties in this respect have given them their well-known usefulness in medicine and in the examination of materials. There is no room here to discuss why penetration should vary so greatly with wave-length. The length of the wave is smaller than the lattice point distances, but it is comparable therewith.

We assume that an electron, when a train of such waves passes over it, is set into forced vibration, so that in turn it becomes itself a source of a secondary train of waves having the same frequency as the primary. In making this assumption we necessarily take no account of the newly discovered slight change of wave length known as the Compton effect : and we are justified in doing so because its influence on the phenomena we are considering is far too small to affect our reasonings and calculations, so far as we shall find it necessary to take them.

If now we suppose a train of waves to pass over a crystal containing many atoms, each atom containing several electrons, a multitude of secondary wave-motions will be set up which will spread away into space. No eye can detect them, but their effects can be measured in the usual way by the ionisation chamber or the photographic plate. We assume that the aggregate intensity of the radiation proceeding from the crystal in any direction can be calculated according to the well-known and well-tried laws of interference. The nett amplitude of the vibration at any point is the resultant of all the amplitudes of the secondary waves which are passing over the point at the moment in question.

Let us imagine a train of waves in the ether as in the figure, advancing and passing by an object that can scatter them ; if we like to take the simplest case we can think of we may say that the object is a single electron. A set of spherical waves will spread out in all directions in space concentric

with the object which is their origin. Just so a set of concentric ripples will spread out on the surface of a pond if a train of waves impinges on a post projecting above the

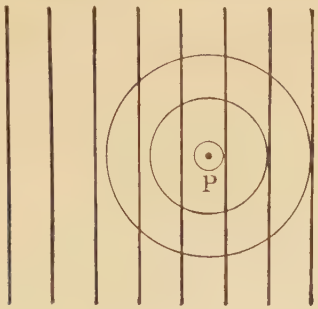


FIG. 4.

surface. What now will happen if there is a set of points arranged in any regular fashion ? Suppose, for example, we have a number of points in one straight line as in Fig. 4*a*.

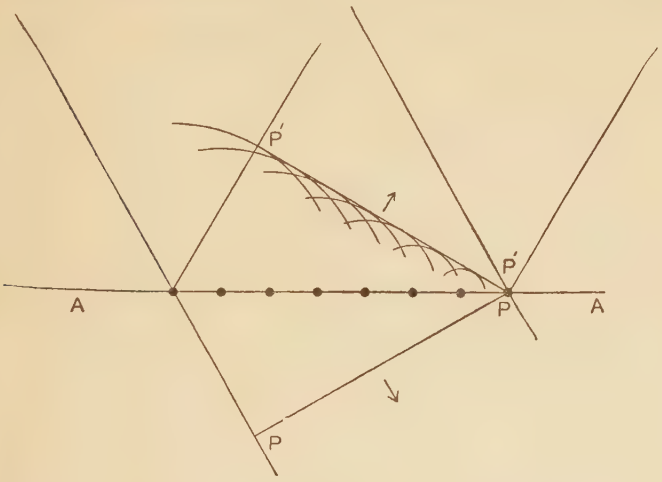


FIG. 4*a*.

When waves are incident upon the row each point becomes the centre of a train of spreading circular waves, and these different trains combine to make linear ripples which recede, as in the figure, making a ' reflected ' train. The rest of the

wave formation from each point spreads away in the usual fashion, dying out rapidly as it spreads over a wider front.

The combined wave front, on the other hand, is not only strong relative to the rest but persists for a far longer time ; if the posts are many and are not too wide apart the reflected ripples are the obvious parts of the phenomenon. In fact, the effect is often seen in a harbour where a row of closely planted piles reflects the oncoming waves. So also the air waves of sound are reflected by a row of palings. This is the one fundamental principle of the new analysis, extended to the case of three dimensions in which a number of points are arranged regularly in space according to some pattern, instead of a row of posts in a straight line. Let us consider this rather more complicated but exactly analogous case.

Suppose that the dots in Fig. 5 are some of the representative points in the solid : each point stands for one unit of

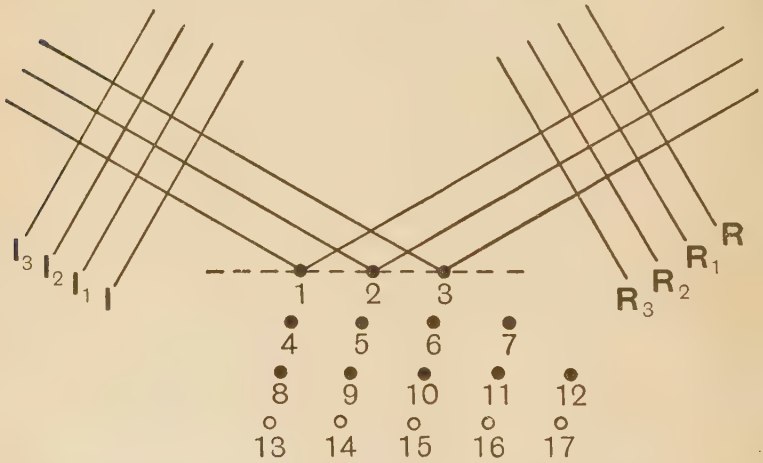


FIG. 5.

pattern. The points marked 1, 2, 3 are a few of the points lying in a plane perpendicular to the plane of the paper ; we suppose ourselves to be looking edgeways at this and parallel planes, in some of which also a few points are marked, such as 4, 5, 6, 7 in one plane, 8, 9, 10, 11, 12 in the next, and so on. On account of the regularity of the pattern it must be possible

to consider the points as arranged on planes in this way, just as in the two-dimensional problem of a vineyard it is possible to think of the vines as in rows in various ways. The points are not all in the plane of the paper, because if they were it would mean that certain point-bearing planes which we are regarding edgeways are at right angles to other point-bearing planes : and this would presume a certain rectangular character in the solid which it does not necessarily possess. The dots in the figure may be projections upon the paper of the representative points, but this does not affect what follows. The regularity with which the dots are drawn is intended to be in conformity with the general regularity of the spacing. Furthermore, only a few points are shown, but these must be taken to represent the enormous number which come into action when the X-rays sweep through the crystal.

Suppose that I, I_1, I_2, I_3 is a train of incident waves ; if they are X-rays they will sweep through the material as waves would sweep over a sheet of water where posts project above the surface. From each of the numbered points secondary waves spread away into space and may lead to the formation of a reflected train. Suppose R, R_1, R_2, R_3 is such a train ; let us take I in the incident train and R in the reflected train as reference lines, and let us suppose also that the waves are perpendicular to the plane of the figure. The condition that combination between the scattered waves from the points 1, 2, 3 shall take place is that the sum of the perpendiculars from point 1 upon the lines I and R is equal to the same sum in the case of points 2 and 3. When this is the case the straight line through 1, 2, 3 obviously makes equal angles with I and R ; this is in fact a particular case of the familiar law of reflection. When this equality is satisfied the sum mentioned is the same for all the points on the plane to which in the figure 1, 2, 3 belong. It is, of course, unnecessary that the points 1, 2, 3 should be equally spaced along the line on which they lie so far as this reflection effect is concerned.

But is there a possible combination which will take in not only points 1, 2, 3 but all the other points in the figure ?

If so the reflection will surely be far greater. Now it is clear that the sum of the perpendiculars from No. 4 is greater than the sum from No. 1, but if that difference is a whole wave-length the combination of No. 4 with Nos. 1, 2, 3 will take place equally well. For what difference can there be between two successive waves of a train ? And if 4 enters into the alliance so also will 5, 6, and 7, because the line 4, 5, 6, 7 is equally inclined to *I* and *R*. Furthermore, owing to the regularity of the arrangement of the points in the figure, 8, 9, 10, 11, and 12 will join in because their contributions are exactly two wave-lengths behind those from 1, 2, 3 ; and 13, 14, 15, 16 because they are three in arrear. In fact, all the points we have put in the figure and all those we have not put will combine ; and, though the contribution of each one may be exceedingly small, the total effect is appreciable. The fine pencil of X-rays which we employ in the actual experiment sweeps over billions of such points in the material, and each makes a contribution to the reflected rays.

Can we arrange that the sum of the perpendiculars on *I* and *R* from No. 4 shall be exactly one wave-length greater than the corresponding sum for No. 1 ? Surely ; for, since

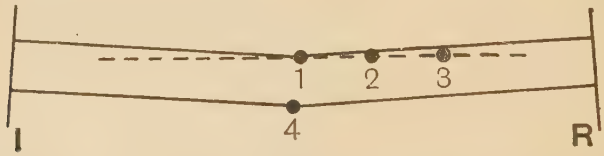


FIG. 6*a*.

we can place the collection of points at a different angle to the incident train, we can make the difference in the two sums less as in Fig. 6*a*, or greater as in Fig. 6*b*, and we can therefore adjust the difference to the desired equality. When the adjustment is made there is combination of all the points in the solid, and an observable reflection results ; when the adjustment is absent, or indeed is only slightly imperfect, there is no combination, and, as we find in practice, no reflection at all. The angle between the direction of the incident rays and 1, 2, 3, and therefore that between the incident and reflected rays, must have a definite value.

It will be observed that the combination effect is only possible because there is regularity in the spacing of the rows

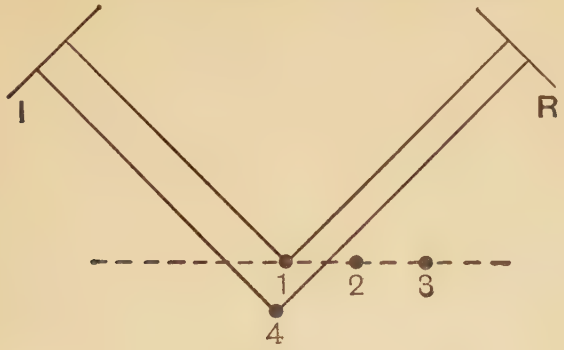


FIG. 6*b*.

1, 2, 3 ; 4, 5, 6, 7, etc. If then a pencil of X-rays having one definite wave-length be represented in Fig. 7 by XC, and if

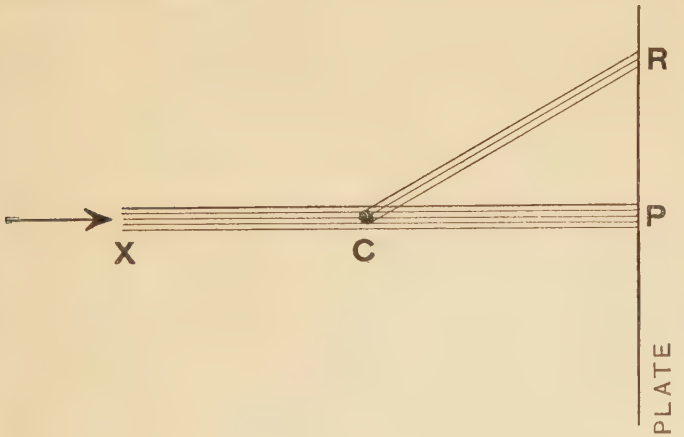


FIG. 7.

a crystal is placed at C so that the X-rays sweep through it, it will be possible to turn the crystal into various positions until suddenly a reflected ray CR flashes out ; when that occurs XC makes as we have seen a certain angle with CR, an angle depending as regards size upon the magnitude of a certain spacing in the crystal.

The condition for a reflection is readily put into mathematical terms. If the rows of dots of Fig. 5 are replaced by lines marked *pp* in Fig. 8, and *C* is some point on the line of a reflected ray where the various incident rays of the figure

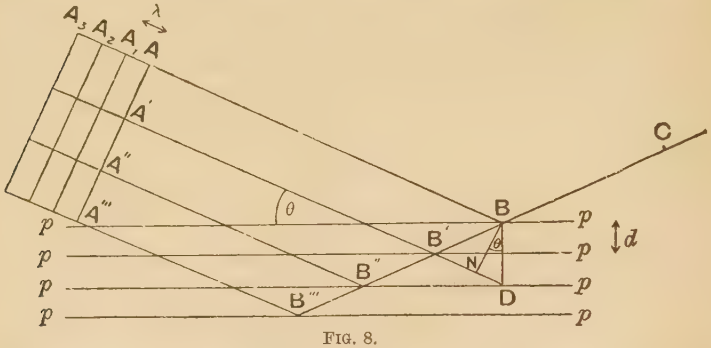


Fig. 8.

combine, then the sum of AB and BC must be less than the sum of $A'B'$ and $B'C$ by one wave-length, or indeed by any whole number of wave-lengths. This difference is equal to

$$\begin{aligned} A'D - AB &= A'D - AN \\ &= ND \\ &= 2d \sin \theta, \end{aligned}$$

which quantity is to be equal to $n\lambda$, where λ is the wave-length, θ is the glancing angle, d is the distance between two successive layers, and n is any integer. According to the value of n, the reflection is said to be of the first, second ... n^{th} order.

When this condition is fulfilled every point in the system conspires to increase the intensity of the reflected ray. If a slight change is made in any one of the three quantities λ, d, θ, the combination breaks down and no reflection is observed. If the secondary wave from one point is out of step with the secondary wave from its immediate neighbour by so little as one thousandth of a wave-length we have only to take two points five hundred times as far apart to find secondary waves in entire opposition to each other, and this is a very small distance in comparison with the dimensions of the irradiated crystal.

The curious difference between the phenomena of the reflection of light by a mirror and of X-rays by a crystal is generally responsible for some of the initial, but merely temporary, difficulties of the new subject. In the former case a ray of any wave-length is reflected no matter what angle it makes with the mirror : in the latter case rays of a given wave-length are reflected by a set of crystal planes if they fall on the planes at the proper angle of incidence, but not unless.

Suppose that a set of waves on a pond passes over an irregular group of posts as represented in Fig. 9. From each

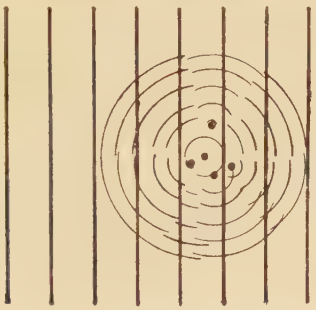


Fig. 9.

post starts out a concentric set of ripples. Round each post is a jumble of wavelets, and the complication is greater if we suppose some posts to be more effective than others. At a little distance from the posts, nevertheless, a ripple of nearly circular form begins to shape itself, and at a greater distance the effect of the group is much the same as that of a single point. The only differences are that the circle is not perfect, and that it is not of the same strength all round. The latter effect is due to mutual interferences between the ripples from the different posts in the group. In some directions there is more interference than in others.

The three dimensional case of X-rays and electrons is exactly analogous. When the X-rays sweep through the unit cell and a fraction of their energy is scattered in the form of secondary waves by the various electrons in the cell, the effect at a little distance is much the same as if a single

electron in the cell had alone been responsible. It is true that the mutual interference of the various electrons causes the resultant effect to be different in different directions. Nevertheless, we can replace the whole unit cell by a representative point, and so the whole of the argument that led to the reflection formula $n\lambda = 2d \sin \theta$ applies as well to the crystal as to the skeleton array of points in Fig. 5. For the essence of the argument consisted in a reckoning of the joint effect of all the electrons in some one direction, and all the unit cells being exactly alike act in exactly the same way in any common direction. Reflections are to be found in the same positions as before : it is only their intensities that are affected by the relative positions of the electrons within the unit cell. It is, indeed, by measuring these intensities, and by comparing the results with those calculated from some assumed structure, the results being expressed in terms of what is known as a structure factor, that we infer the positions of the atoms within the cell. That, however, belongs to the later stage of our enquiry : in the present stage we think only of the space-lattice of the crystal, each point on the lattice representing a unit cell.

Suppose then that a small crystal, let us say a diamond, is placed in a beam of X-rays, so wide that the crystal may be said to be bathed in them ; and suppose that the rays are homogeneous, only one wave-length being present : to fix our ideas let this length be one Angstrom Unit. There will be no reflection except by a most unlikely chance. Sets of parallel equally spaced planes can be drawn through the points of the diamond lattice in an infinite number of ways ; but it is not to be supposed that any one of the sets of planes will make with the incident rays the angle which is required if waves of the given length are to be reflected by a set of planes of a given spacing. Only a small number of the different sets will be able to reflect at all, because the spacing is generally too small to make a difference of a whole wave-length in the rays reflected by successive planes no matter how great the incident angle may be. Clearly, the spacing must be greater than half a wave-length ; that is to say, half an Angstrom

Unit in this case. As a matter of fact there are only fifteen sets of planes in the diamond which are able to reflect the wave-length we have chosen, and in each case if there is to be reflection the set must make with the incident ray the angle proper to that set as defined by the formula above. If we turn the diamond round some axis a certain number of the planes will, each in its turn, make with the incident ray the angle which will bring about a reflection. It is always the body of the crystal that is concerned in the reflection, the form and condition of the surface have little influence. The whole of the body does not act with equal effect because the rays lose their strength in making their way through the crystal, especially when reflection is taking place and reflected energy is abstracted from that of the incident ray. Experiment shows that the total intensity of the reflection due to any set of planes is not proportional to the weight of the diamond, but tends to become proportional thereto as weight is reduced.

Whenever we measure the angle of reflection of the incident rays by a given set of planes we can calculate the spacing of the planes by means of the formula given above. If we do this for three sets of planes which do not all meet in parallel lines, or in crystallographic language, do not belong to the same zone, we can calculate the constants of the lattice, provided that we have observed, as we can do in the course of the same measurements, the angles that these sets of planes make with each other ; for, it will be remembered, the unit cell can be drawn in an infinite number of ways, and its six faces can be parallel in pairs to any three such sets of planes : and if any form of the cell is known all other forms are known. It must, however, be observed here, in order to avoid future confusion, that the spacings of three sets of planes which are to provide the faces of the unit cell cannot be determined without ambiguity unless the spacings of other planes are measured at the same time. The explanation of this will appear very soon, and indeed we must consider it very carefully, because it is more than a mere explanation, it is an important principle in the development of

the subject. But we can postpone this point ; all that we need for the moment is the recognition of the fact that in the end the spacings of the three sets of planes can finally be determined.

If we carry out our experiment with our crystal only as far as this we have gone further than we have ever been able to do by the usual measurements of the angles between the faces made on the optical goniometer. For we have not only measured the proportions between the lengths of the edges of the lattice cell, however drawn, which is all that goniometry can do, but have determined their lengths absolutely. We now know the volume of the unit cell, and, with a rough knowledge of its specific gravity, can calculate the contained mass with sufficient accuracy to give us the number of molecules it contains, which number of course is an integer.

When the results of an X-ray determination of this kind are compared with those obtained by the older methods it is always found as might be expected that the two determinations of the angular dimensions of the lattice are in agreement. Also, the ratios of the linear dimensions of the lattice as found by X-rays are commensurable with those found by aid of the goniometer ; but they sometimes show that the latter are in error in doubling or giving some simple multiple or submultiple to one or other of the ratios of the sides of the cell. For instance, the ratios of the axes of the monoclinic crystal naphthalene tetrachloride are given by v. Groth to be 0·7673 : 1 : 0·7004, whereas the actual lengths of the edges of the corresponding cell are 7·88, 10·30 and 14·2, and these are in the ratio 0·765 : 1 : 1·377. The explanation is simple : there is a certain arbitrariness in the choice of the ratios from goniometric measurements, because the choice is determined only by the wish to associate the principal faces of the crystal with the more important planes of the lattice, whereas the X-ray measurements are absolute.

The interpretation of the above measurements may be said to complete the first stage of crystal analysis by the new methods : it results in the determination of the lattice. The

volume and form of the unit cell are now known; but nothing has yet been done to determine the arrangement of the cell contents. That comes at a later stage.

The apparatus which is employed for the measurement of the angle of reflection is simple in principle, because it has a simple duty to perform.

For example, the apparatus required for the method of the ionisation spectrometer consists of no more than an X-ray bulb producing a pencil of X-rays of definite wave-length, a table on which the crystal can be placed and turned into any position, and an ionisation chamber for the detection of the reflected pencil. In Laue's original method a pencil of heterogeneous X-rays is passed through a single crystal: the numerous reflected pencils are received on a photographic plate and produce upon it a number of spots. The rotating crystal method employs a pencil of homogeneous rays, a single crystal in uniform rotation, and a photographic plate. In the powder method the substance in the form of powder is traversed by a fine pencil of homogeneous X-rays, and the photographic plate shows, on being developed, a number of rings. We must consider these four principal methods, because each has its advantages and disadvantages. It is generally convenient to use two or more in conjunction. We shall illustrate the use of each method by one or more suitable examples.

Meanwhile, we must for a moment pay attention to our nomenclature. Presently we shall have to consider and compare the reflections by various sets of planes, and must therefore, as crystallography has always done, adopt some means of describing the planes in reference to the particular unit cell which has been chosen. We take a point O on the lattice as origin of reference, and join the origin to three neighbouring lattice points A, B, C by straight lines which are to form contiguous edges of the unit cell. The cell must, of course, contain no lattice points; such points should be found at its corners only.

As we have already seen, sets of uniformly spaced planes, each set containing all the points of the lattice, can be drawn

in an infinite number of ways. A set is completely defined by its spacing and its orientation with respect to the crystal. A set must, being uniformly spaced, divide any straight line joining two points of the lattice into a number of equal parts. Let the set dividing OA into h parts, OB into k parts and OC into l parts be called the (h, k, l) set, or, to use the common expression, the (hkl) plane. When h, k, l are all positive integers the intercepts are simultaneously positive or simultaneously negative. If one of them, say l, is negative, the intercepts on OA and OB are positive when the intercept on OC is negative, and *vice versâ*. In mathematical language, if $OA=a$, $OB=b$, $OC=c$, and OA, OB, OC be taken as axes of reference, the equation of any plane of the set is

$$\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}=\text{an integer.}$$

That plane which goes closest to the origin without going through it is

$$\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}=1.$$

In Fig. 10 various sets of planes are shown. A (432) set of planes divides OA into four parts, OB into three, OC into

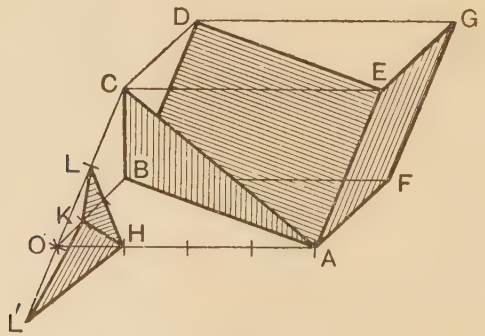


FIG. 10.

two. HKL is a member of this set. A $(43\bar{2})$ set is also shown, illustrated by the plane HKL'. The (111) set, illustrated by ABC, sub-divides none of the edges, and the (100)

set, illustrated by $AFGE$, does not cut the y or z edges at all; it is parallel to the plane OBC. $AEDB$ belongs to the (110) set.

Let us take as particular examples the most important sets of planes belonging to the simple cubic lattice. In Fig. 10*a* $OABCDEFG$ is a cube, and its corners are points on

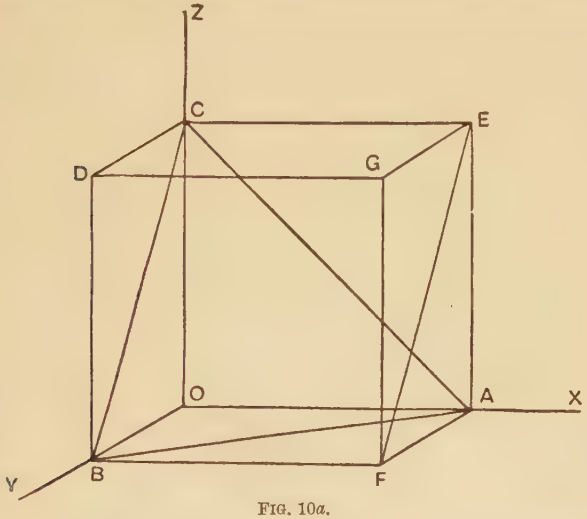


FIG. 10*a*.

the lattice, so that the cube is the unit cell. We take OA, OB, OC as axes of x, y, z respectively. Then the (100) planes are all parallel to the plane containing O, B, D, C; which four points lie on one member of the set and A, F, G, E lie on a consecutive member of the set. The spacing of the set is OA. Similarly, the (010) set is parallel to the plane $OAEC$ and the (001) to $OAFB$.

The points C, E, F, B lie together on a member of the (011) set: adjacent members pass through D, G, and O, A respectively. All the members are alike in regard to their content of lattice points, though they do not contain equal numbers of those that are shown in the figure. The spacing is equal to the cube edge divided by $\sqrt{2}$, say $OA/\sqrt{2}$. Similarly, the (101) set is parallel to the plane $CDAF$, and so on. The set parallel to the plane $OBGE$ is denoted by $(10\bar{1})$. There are six sets of planes having the same spacing $OA/\sqrt{2}$.

Again, the points A, B, C lie in a member of the (111) set. The spacing is the perpendicular from O on ABC, *i.e.* $OA/\sqrt{3}$. Consecutive members pass through O, ABC, DEF, G respectively ; and all are equally rich in lattice points. The $(11\bar{1})$ set is parallel to ODE : and so on. There are four of these sets.

There are two other lattices to which the name ' cubic ' is given though they do not truly deserve it. For the purpose of comparison the three cubic lattices are shown in Fig. 11. The first of the three is the simple cubic lattice which we have just considered.

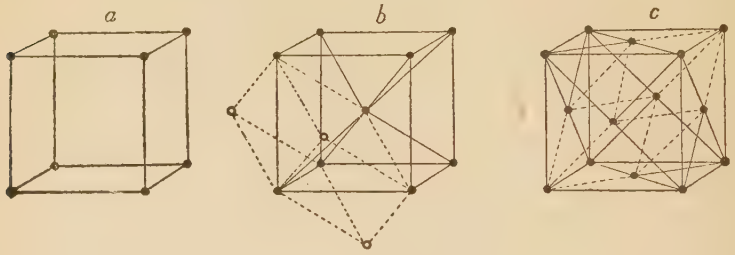


FIG. 11.

The next (Fig. 11*b*) is the body-centred cubic. If we place at the centre of each unit cell of the first kind a lattice point representing exactly the same collection of atoms and molecules as does each of the points at the corners of the cell, we double the number of lattice points in space, though not the number that are represented in the figure. The cubic cell is no longer the unit cell because there are now two lattice points to the cube. The dotted lines in Fig. 11*b* represent one way of drawing the unit cell, but of course there are many more. The body-centred lattice is of common occurrence ; it is, for example, the lattice of ordinary iron. The crystal is a cubic crystal, though the unit cell is not cubic ; and it is convenient to retain the cube edges as axes of reference, and the corresponding nomenclature of the sets of planes. Thus, we still refer to the set of planes parallel to the yz plane as the (100) set. But the spacing is no longer equal to the cube edge : it is halved. The new

points lie on planes which are half-way between the old planes ; as we say, the old planes are interleaved. Moreover, the new planes are just as rich in lattice points as the old, so that the (100) planes now consist of a set of similar planes, all parallel to one another and separated by a distance equal to half the spacing of the old. It is convenient to express the fact by saying that the (100) reflection and all (h00) reflections, h being odd, have vanished. The reflections for which h is even remain.

So also, the (111) reflection disappears because the new point at the centre of the cell is exactly half-way between two members of the old set of (111) planes, viz., those which contained the points *ABC* and *DEF* respectively.

Thirdly, there is the so-called face-centred cubic lattice. It is formed by adding three lattice points to the simple cubic cell (Fig. 11*a*) : new points are placed at the centres of the six cubic faces. A point so placed is shared between two adjacent cubic cells, so that only part of what it represents belongs to the cube : the other part of what a point represents is brought into the cell by the lattice point in the opposite face. Thus the six face centres represent the addition of three new points. The cell is shown in Fig. 11*c*. The cubic cell is not now a unit cell, for such a cell can only contain or represent one lattice point : one form of the unit cell is shown in the dotted lines of the figure.

In this case also, it is customary to use the edges of the cubic cell as axes of reference. The (100) planes are still therefore the planes that are parallel to one of the cube faces. The new points have doubled the number of points of the old planes, and also interleaved them by planes of equal richness. The spacing is halved, as it was in the case of the body-centred cube. The (110) planes are also halved for similar reasons. The (111) planes are each of them four times as rich as they were before, and there are no new planes : the spacing of this set is the same as that of the simple cube.

A longer list of the spacings of the three varieties is given in the last chapter of this book, where it is required in con-

nection with certain problems to be solved. What we have done now we shall find useful at once.

There are no other ways of adding lattice points to the single cubic cell, when it is a condition that the new points are to be exactly like the old in their surroundings. We might add more points but they could not represent the same things.

CHAPTER II

METHODS OF ANALYSIS

LAUE'S method of showing the diffraction of X-rays by a crystal requires that the rays shall be heterogeneous, such, for example, as are emitted by a tungsten anticathode when bombarded by electrons having velocities due to, say, seventy thousand volts. Under such circumstances there is a quantity of general radiation of wave-lengths ranging from about 0·18 to 1·00 Angstrom Units, with a maximum at about 0·25 A.U. The crystal is at rest during the exposure of the plate. The angle between the incident pencil and each set of planes in the crystal is therefore a fixed quantity as well as the spacing on the planes. The flexibility required in the relative values of d, λ and θ, if the equation $n\lambda = 2d \sin \theta$ is to be satisfied, is supplied in this case by the variability of λ.

Let us suppose that a narrow pencil of X-rays is passed through a thin sheet of rocksalt in a direction which is perpendicular to a cube face. The pencil must be narrow, or, alternatively, the crystal must be small if the spots on the photograph are to be reasonably fine.

The resulting photograph is shown in Fig. 12, Plate II. Each spot is due to the reflection by one set of planes ; and every set within a given range shows a reflection.

The figures 13, 13*a* and 14 are intended to illustrate the production of the spots in the photograph. In Fig. 13*a* the crystal and X-ray pencil are represented by a small cube and a rod. In Fig. 14 the cubic figure represents a unit cell the edges of which are parallel to the edges of the cubic crystal of Fig. 13*a*. Suppose that the incident pencil of X-rays is parallel to CO, and the photographic plate to the plane OAB. Consider some set of planes, *e.g.* that of which $C''AB$ is one ; it is, say, the $(3\bar{3}1)$ set of

which consecutive members pass through O, C, C', C'', etc., and divide OA and OB into three parts, OC into one, if such an expression is allowed for the sake of continuity. The reflected ray proceeds in a direction which makes the same

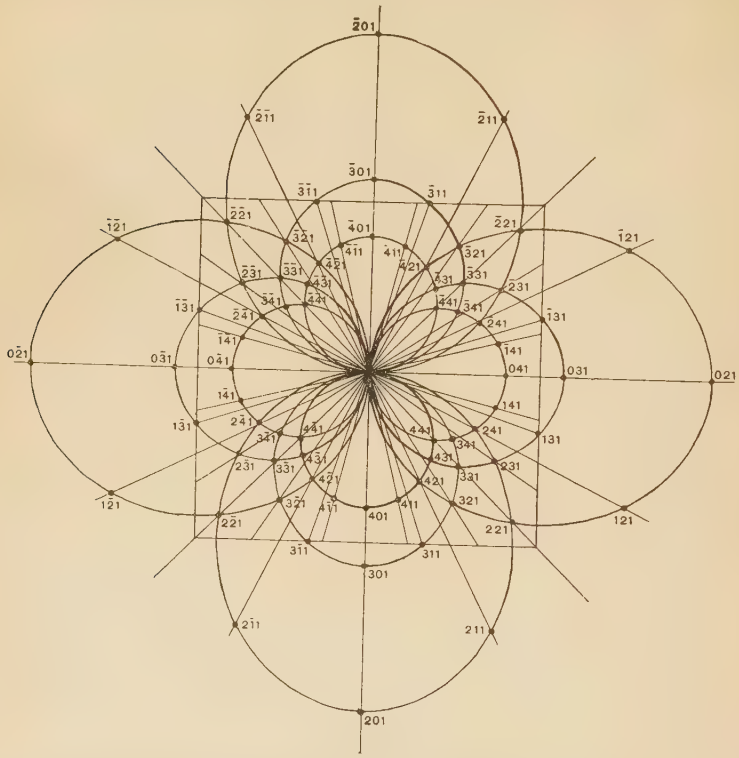


Fig. 13.

Figs. 13 and 13a.—Drawings from a model showing the process of the Laue photograph. In 13a the rod represents the incident X-rays, a small cube the crystal and strings going to various points of the base the rays that make the corresponding spots. Fig. 13a a side drawing of the photograph.

angle with the plane $C''AB$ as does the incident ray ; and the wave-length of the ray is such as to satisfy the general law $n\lambda = 2d \sin \theta$. Here d is the spacing of the set of planes ; it is the perpendicular from O on that member of the set which goes through C. The angle between the plane and either the incident or reflected ray is the angle θ, and λ is the wave-length automatically selected from the incident

radiation to fit the equation. As n may be any integer, more than one wave-length may be selected; all the selected radiations, since they are reflected by the one set of planes, travel in the same direction. In this case the reflected ray must lie in the plane containing OC and OD, and the corresponding spot on the diagram of Fig. 13a is therefore found

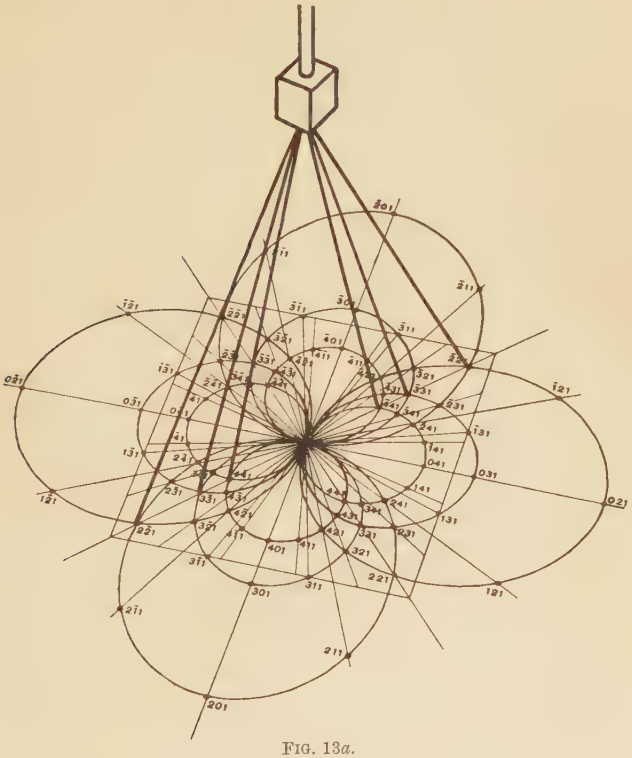


FIG. 13a.

on the diagonal of the square in the model. The position of the (221) spot is also marked, and that of the (441). The latter, however, did not appear on the photograph from which the drawing of Fig. 13 was made, because the general radiation did not contain radiation of short enough wave-length. As the figures designating the planes become larger the spacings become less, and smaller wave-lengths are required

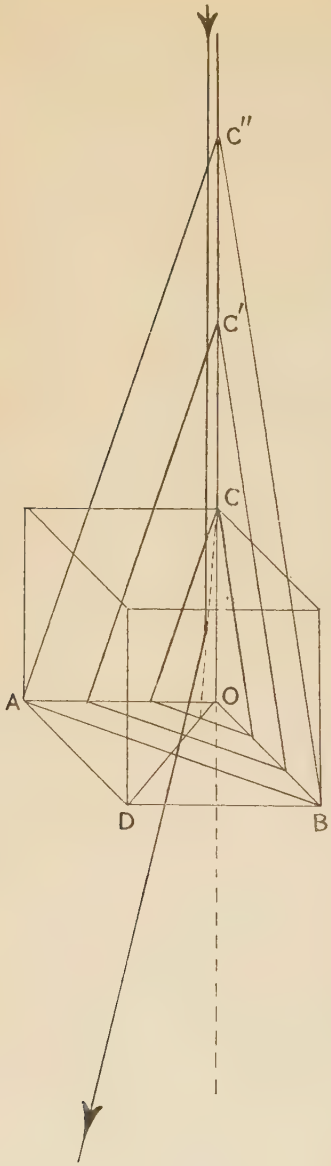


Fig. 14.

for the fulfilment of the reflection law. There is a blank space in the middle of the Laue diagram, not because there are no planes capable of reflecting into that space, but because there is no incident radiation of sufficiently short wave-length. On the other hand many planes contribute no spots because their reflections fall beyond the limits of the plate.

It will be observed that spots have a tendency to be disposed on ellipses which pass through the central point. For this there is a simple and very interesting reason. Consider the various sets of planes that are parallel to $C''A$; in crystallographic language planes belonging to the zone parallel to $C''A$. The description of any one of the set is $(3k1)$, where k is any integer. One plane of each set passes through the points C'' and A. We have already found on the diagram the spot due to (331). If now we look for the spots due to the other sets of this zone, viz. (301), (311), (321), etc., we shall find them all on one of the ellipses on which the spot (331) already lies. The reason is that in each case the reflected and incident rays make equal angles with the reflecting planes and therefore

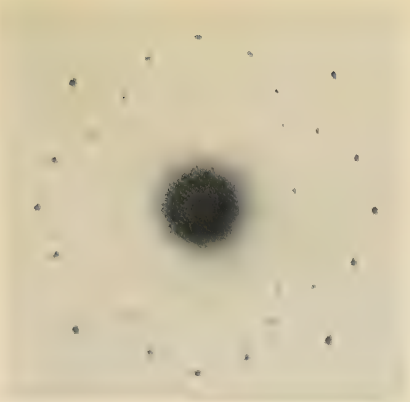


FIG. 12.—Laue photograph of rock salt. The outlying spots on the vertical and horizontal lines are (301) etc. (See Fig. 13.)

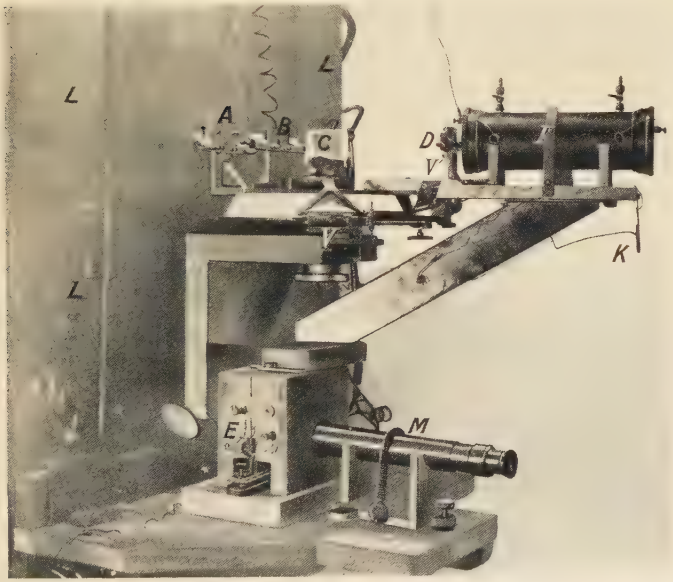


FIG. 16.—X-ray spectrometer.

LLL, Leadbox.
A, *B*, *D*, Slits.
C Crystal.
I, Ionisation chamber.
V, Vernier of crystal table.
V', Vernier of ionisation chamber.
K, Earthing key.
E, Electroscope.
M, Microscope.

with any straight line in those planes, and therefore with $C''A$. Consequently, if we imagine a plane to pass through $C''A$, or a parallel to that line passing through O, and to be turned round that line as axis, it will become in turn a member of each of the sets already mentioned : and the reflected ray will always make with $C''A$ the angle which the incident ray makes with it. This being a constant quantity the reflected ray will always lie on a circular cone which has for its axis a line through the crystal parallel to $C''A$ (Fig. 14). The cone meets the photographic plate in an ellipse ; on which must lie every spot due to reflection from any set of planes to which $C''A$ is parallel.

It will be observed further that the spots vary widely in their intensities. If we think only of a space lattice as a set of points we may find it difficult to understand why one set of planes should reflect better than another, since every set includes all the points. But we must remember that we have as yet taken no account of the ' structure factor ' already described (p. 18). Presently we shall find that this is a very important matter ; for we rely on these differences of intensity to tell us of the actual distribution of the sources of the scattered radiation about the points of the lattice. That is to say, we hope to learn through them the arrangement of the atoms in the crystal. They are our main help in the latter stages of our work.

The Laue photograph, by itself, is not easy to decipher. The wave-length of the radiation to which each spot is due is unknown at the outset, and therefore the fundamental equation cannot be used. The positions of various reflecting planes can be found, but their spacings cannot be found directly. Also, the various orders of reflection by any one plane are not separated, and valuable information is therefore hidden. The photograph does, however, give useful information respecting the symmetry of the crystal, and the method is of great help when employed in conjunction with others.

The method of the ionisation spectrometer has its own

interest and usefulness. The instrument was originally designed to measure one at a time the reflections of the X-ray beams by the different sets of planes within the crystal, thus making the simplest application of the law, $n\lambda = 2d \sin \theta$, which W. L. Bragg had formulated. A narrow pencil of X-rays is defined by a convenient system of slits and is

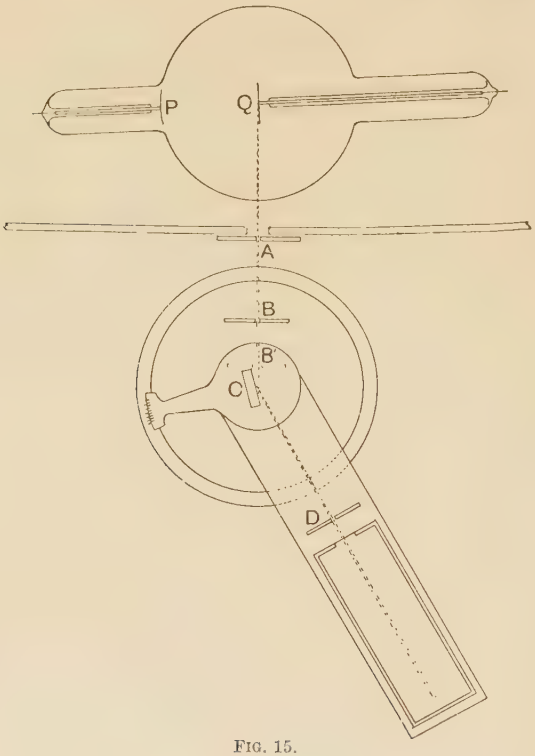


FIG. 15.

allowed to fall upon a crystal face. The crystal is mounted upon a rotating table, the orientation of which is measured by scale and vernier in the usual way. The reflected ray, when there is one, is received in an ionisation chamber, filled with a gas which responds readily to the action of the rays. If, for example, the target in the X-ray bulb is of rhodium or molybdenum, it is convenient to fill the chamber

with the vapour of methyl bromide, because the characteristic rays of either of these metals are strongly absorbed by bromine, and produce correspondingly strong ionisation. The ionisation chamber is insulated and connected to one terminal of a high potential battery : an electromotive force of two hundred volts is sufficient. An electrode is mounted in the chamber, just out of the way of the rays which enter it, and is connected through a mounting in an amber plug with a wire leading to some form of electroscope. The details of the arrrangement are shown by the two accompanying figures ; of which Fig. 15 represents the plan of the reflecting system and Fig. 16, Plate II, is from a photograph of the spectrometer. These illustrations are taken from *X-Rays and Crystal Structure*, a book written in 1915 in order to explain the new method of analysis. Although they do not show the improvements which experience has since suggested, they show all the essential features, and their simplicity makes them easy to describe. The X-ray bulb appears in the upper part of the first of the illustrations. The thin plate at Q is now replaced by a solid metal block, water-cooled in order to stand a heavy discharge, and the aluminium cathode is replaced by the hot wire filament of Coolidge. The rays which are employed leave the block almost tangentially, so as to give a line source. The slit at A is attached to the wall of the large lead box which contains the bulb : the lead serves to protect the worker and at the same time to prevent disturbances of the measuring apparatus due to stray radiations. The crystal is shown at C : it appears in the illustrations as a large block, because in the first measurements a relatively large crystal was employed, mounted so that the face under observation contained the axis of the rotating table on which the crystal was mounted. The slits A, B and D define the rays before and after reflection. The ionisation chamber revolves about the same axis as the crystal, and its positions are similarly recorded. The angle between the directions $QABC$ and CD is twice the glancing angle θ ; the crystal face is equally inclined to these directions. In the use of the instrument the ionisation current

is measured for a series of settings of the instrument, such as that of the figure : the angle θ is altered by successive steps of convenient size, the spectrometer moving twice as fast as the crystal.

If the incident rays are monochromatic, of wave-length λ, and the spacing of the planes parallel to the crystal face is d, there is no movement of the leaf in the ionisation chamber unless the law of reflection is fulfilled, viz. $n\lambda = 2d \sin \theta$, where n is an integer. If λ is known, and θ is measured, d can then be calculated. When the target of the X-ray bulb is bombarded by electrons emitted from the anticathode under a suitable potential the rays emitted by the bulb consist largely of the characteristic rays of the metal, together with a small amount of general radiation, that is to say, of rays ranging continuously over a whole series of wave-lengths. For instance, if a potential of about 30,000 volts is applied to a molybdenum tube there is a relatively strong emission of the following waves (together with others much feebler) :

α_2	-	0·712 strong,	β	-	0·631 moderate,
α_1	-	0·708 very strong,	γ	-	0·620 weak.

Very little confusion is caused by the presence of so many different wave-lengths, because α_1 and α_2 are not generally differentiated from one another in the ordinary work of crystal analysis, γ is very feeble, and β cannot be confused with α if simple precautions are taken. The β radiation can indeed be greatly reduced in intensity, as compared with the α, by the use of a suitable absorbing screen ; but this is rarely advisable, since the intensity of the α radiation is also reduced, though not in proportion, by such a screen. With the voltage named the general radiation is weak as compared with the α and β lines : with lesser voltages the contrast is less apparent, and the lines no longer show up sufficiently when the voltage falls below 20,000 volts.

It is by no means the general case that a crystal possesses a large face as represented in Fig. 15. Sometimes a face can be prepared by grinding, and this is especially the case with such substances as calcite, quartz and other minerals. More

often it is necessary, or at least convenient, to examine a crystal which shows no natural face parallel to the set of planes under consideration. Crystals of organic substances, for example, are often so small that it is impracticable to prepare the faces that are required. A small crystal is then mounted as centrally as possible on the axis of the rotating table, being held in some convenient way. The slits at A and B are opened to such an extent that the crystal is completely bathed in the X-rays in all positions of its rotation. The slit at D, which limits the entrance of the reflected rays into the ionisation chamber is also opened considerably as the position of the chamber is no longer measured. It is only necessary to set the chamber approximately and to adjust the crystal so that it gives the reflection required. The position of the crystal is then observed. A measurement of this kind is made on both sides of the zero position, so that errors of zero are eliminated. When the crystal is small, and the absorption of the X-rays is so little that the whole body of the crystal is contributing nearly equally to the reflection, the result is very accurate. A few quickly made observations, for example, will give the measurement of the spacing of any one set of planes with an accuracy much better than one per cent., relative to other measurements on the same instrument : and this is amply sufficient for most purposes. Far higher accuracies are obtainable if required : more elaborate modern instruments give results which compare favourably with those of optical spectrometry.

It is an interesting point that as θ approaches 90° the

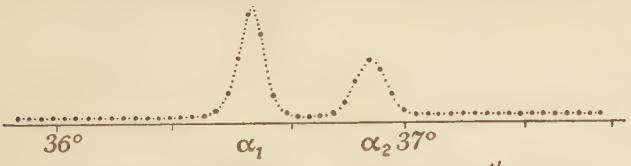


FIG. 17.

resolving power of the spectrometer increases without limit, because a considerable change in θ causes only a small change in sin θ. This effect is illustrated in Fig. 17, which shows

a certain set of observations of the α_1 and α_2 lines in the rhodium spectrum in the fourth order of reflection by the (111) set of planes of diamond, or, more simply expressed, by the (444) planes. Each of the larger black spots represents an actual measurement. The angles of reflection, which are the angular settings of the crystal table, are plotted as abscissae : the ordinates are the currents of the ionisation chamber. The wave-lengths of the two lines are 0·6163 A.U. and 0·6121, so that the separation in the figure is due to a difference of 0·0042 A.U. only.

The ionisation spectrometer measures not only the spacings of sets of planes but also the angle between any two sets : this is one of its most important qualities. The crystal is usually so mounted on the rotating table that the axis of rotation is parallel to an important edge, and therefore to a line joining a point on the lattice to some near neighbour. Such a line will lie on many of the important planes in the crystal, and the zone of which this line is the axis is an important zone. The spectrometer can then be conveniently used to measure the spacings of planes in the zone and the angles they make with each other. If the spacings and the angles of a second zone be measured the combined observations are sufficient for a determination of the cell dimensions.

The spectrometer lends itself readily to the exact measurement of the spacings and orientations of a moderate number of crystal planes. It is also peculiarly fitted for measurement of the intensities of the various reflections. The photographic methods do not allow measurements to be made of orientations, and they have not so far given easy measurements of intensities, though it seems likely that in the future they will be more effective in this respect. Even in respect to accuracy of measurment of individual spacings they are not readily capable of as high an order of accuracy as the spectrometer. On the other hand, the photograph gives a survey of all the many reflections, if sufficiently strong, from planes within limits set by geometrical conditions. In the use of the spectrometer it may happen that, since there are so many planes to choose from, and only one can be under

observation at one time, some one or more of special significance may be passed by without observation, at any rate in the first stages of the analysis. A comprehensive survey is therefore of great advantage.

The method of the rotation photograph which we will next consider is especially useful. A crystal is mounted as at C in Fig. 18, and is made to revolve about a vertical axis. A horizontal pencil of monochromatic rays is made to impinge on the crystal, the pencil being limited by a fine cylindrical aperture or in some cases a slit. The diffracted pencils fall on a flat plate P, or on a cylindrical film F, the axis of the

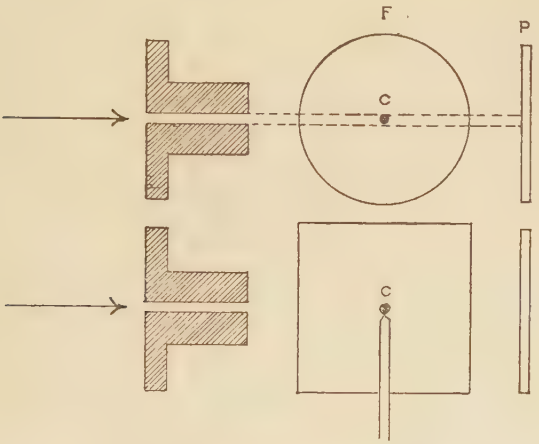


FIG. 18.—Diagrammatic plan and elevation.

cylinder coinciding with the axis of rotation. As the crystal revolves one set of planes after another is brought to such an angle θ with the incident rays that the law of reflection $n\lambda = 2d \sin \theta$ is fulfilled and reflection takes place. An impression is made on the plate by the reflected ray, and the plate when developed shows therefore a collection of spots due to the various planes that have passed through favourable positions. Specimen photographs are shown in Figs. 19 and 25, Plate III, 85, etc. It will be observed that the spots lie on ordered lines, and we must consider what are the occasion and the meaning of the regular array. See also Figs. 101–105.

To begin with, a plane comes to a position of reflection, if it reflects at all, four times in the course of a complete revolution. Since the crystal turns right round there can be no difference between right and left: whatever appears on the right-hand half of the plate must also appear on the left. And, again, though a crystal can possess polarity along an axis such as the axis of rotation, yet X-rays are unable to

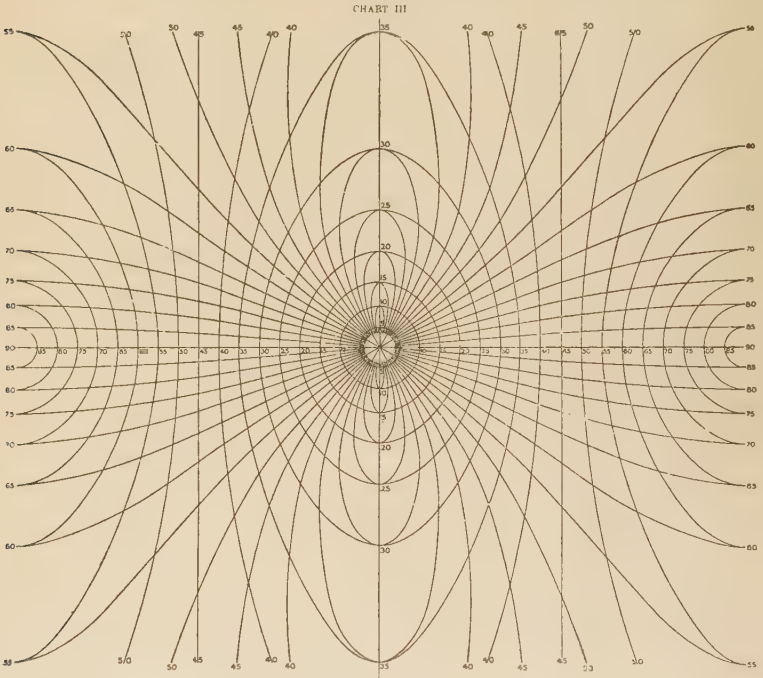
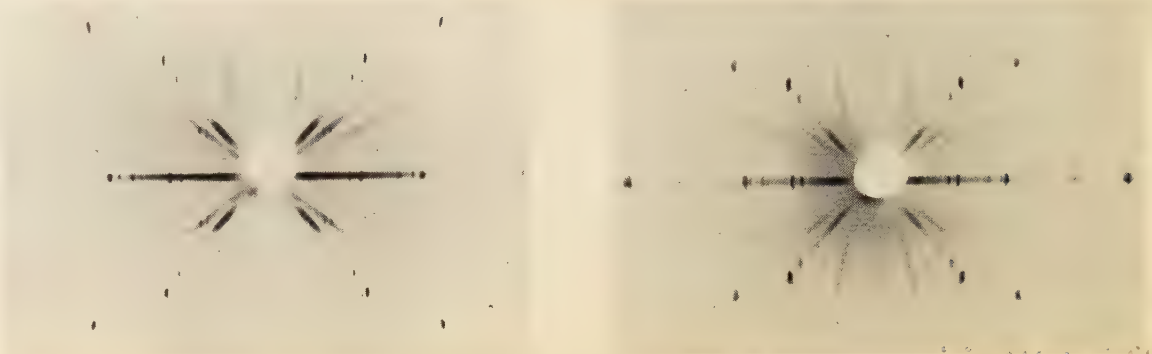


FIG. 20.—Bernal, *Proc. Roy. Soc.* 113, p. 117.

distinguish it, as we shall see later (p. 103), so that the photograph must also be symmetrical about a horizontal line. It is in fact a geometrical proposition that if a plane revolves continuously about an axis which is neither normal to the plane nor parallel to it, any inclination of the plane to a straight line perpendicular to the axis is repeated four times during the complete revolution. The four spots belonging to any one set of planes lie at the corners of a rectangle. If the

FIG. 19.—Rotation photograph of benzoic acid about the *c*-axis.

FIG. 55.—Quartz (twinned on 521) Brazil ?
Photographed by permission from the specimen in the British Museum.



FIGS. 25*a* and 25*b*. Rotation photograph of Na Cl and KCl about the cube edge. The essential difference is that there are spots on the

PLATE III

distance from the centre of any rectangle to the corner is denoted by r, and the distance from the crystal to the plate or film by D, then in the case of the plate r/D is equal to tan 2θ, where θ is as usual the glancing angle. It is often convenient to lay over the plate a transparent sheet on which a series of concentric circles has been drawn, so that r can be read off at once : if in a series of experiments with the same instrument the values of λ and D are always the same the circles may be marked so as to give the spacings directly. If the cylindrical film is used instead of the flat plate the lines of equal spacing are no longer circles, but have the form of the closed curves in Fig. 20. A transparent sheet on which these figures have been drawn or photographed can be used in this case.

The process of naming each spot in reference to the crystal cell is much more laborious.

It may be that the crystal has already been examined on the goniometer and certain directions in the crystal have been chosen as axes, or it may be that the crystallographer has not hitherto given it consideration. In either case it is natural to choose for the axis of rotation an edge or direction which looks important : we will suppose it to be one of the axial directions of the crystallographer or, if the crystal is new, a direction which we are going to take as that of one of the axes, say the axis of c. Such a direction is necessarily parallel to the line joining a point on the lattice to a neighbouring point, not necessarily the nearest of such points, but certainly one among the few nearest points. Suppose that O, P in Fig. 21 are the two points ; when the crystal is mounted on the axis of rotation they are in the same vertical line. Their distance apart is usually a few Angstrom Units. The lines MP and $M'O$ represent incident X-rays.

As the crystal revolves, various planes, each containing the axis of rotation OP, will in turn give reflected rays. The impression made by the pencils reflected by these planes will all lie on a horizontal line across the middle of the plate, because the planes are all vertical during the whole revolution of the crystal. In other words, the spots on this line,

generally called the equator line, are due to planes $(hk, k, 0)$, where hk may have any integral values. See, for example,

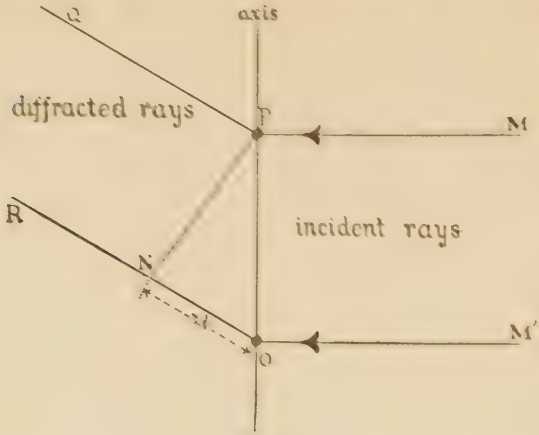


FIG. 21.

the drawing in Fig. 26. If the angles and proportions of the crystal have been previously measured by the ordinary

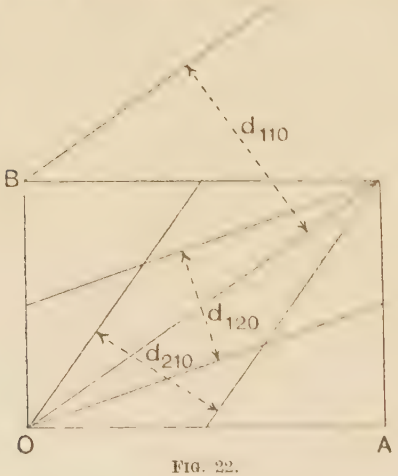


FIG. 22.

goniometer the various equatorial spots are readily assigned to their proper planes, because the *relative* values of the

spacings can be calculated and compared with those that are now observed. If, for example, the cell is orthorhombic, and the axial ratio $a : b$ is known ; and if the crystal is rotated about the c axis, the spots observed will have spacings in the proportion

$$a : b : ab/\sqrt{a^2+b^2} : ab/2\sqrt{a^2+b^2/4} : \ldots$$

or multiples or submultiples of these proportions (Fig. 22). These quantities are the spacings of (100), (010), (110), (120). Thus it becomes known whether any plane gives a reflection, and if so what is the relative intensity of the reflection. Such data are required for an enquiry into the disposition of the atoms within the cell. If the measurements in the zone have already been made on the ionisation spectrometer the spots are still more easily identified.

The other spots in the photographs are obviously arranged in lines across the picture : in the case of the plate the lines are flat hyperbolas, if a circular film has been used they are straight lines. The origin of this arrangement can be explained in the following way.

We remember that rays contributing to a reflected pencil, and coming from different points on the lattice, differ from one another in phase by a whole number of wave-lengths, *i.e.* by $n\lambda$ where n may be zero or any integer. In Fig. 5 all the rays coming from any point in the top layer are alike in phase after reflection, and their phase differs by one wave-length from the phase of those coming from any point in the layer immediately below, by two wave-lengths from the phase of the rays from points in the second layer, and so on.

Now we have seen that all spots on the equator (see Fig. 21) are due to sets of planes, such that O and P lie on one and the same plane of the set : in other words, the planes are parallel to the c axis and denoted by $(hk0)$. The rays coming from O and P, and going to make any spot are in the same phase. The length OP is, of course, exceedingly small in comparison with the distance from the crystal to the plate.

There are, again, other sets of planes for which the rays

from O and P differ by one wave-length, so that O and P lie on consecutive members of the set. These sets, therefore, divide the c axis, OP, into one part only, and their general form is $(hk1)$. If OR and PQ represent the rays from O and P going to make a certain spot under these conditions—they are drawn parallel to each other because the distance to the plate is very large compared to OP—and if PN is drawn perpendicular to OR, then $ON = \lambda$. The angle ϕ between the reflected pencil and the axis of rotation is

$$\cos^{-1} ON/OP = \cos^{-1} \lambda/c,$$

which is a constant quantity. Thus the reflected ray due to a set of planes $(hk1)$, where hk are any integers, lies on a cone, the axis of which coincides with the axis of rotation. The intersection of such a cone with the flat photographic plate is a hyperbola, and with the cylindrical film a circle which becomes a straight line when the film is unrolled. Thus all $(hk1)$ spots lie on the lines next to the equator and on either side of it.

Similarly, rays from O and P, directed so that $PN = 2\lambda$, go to make a spot due to a plane of the form $(hk2)$: because

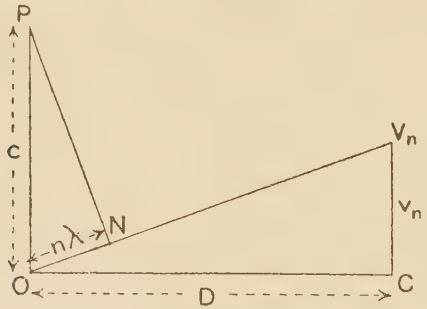


FIG. 23.

O and P, when their phases differ by 2λ, lie on planes of a set which are next but one to each other, so that the set divides OP into two parts. And so on. These separate lines are often called ' Layer lines.'

This peculiar disposition of the spots gives a very good

method of finding the length of OP, that is to say of the axis c. We measure the distance of the vertex of any one of the hyperbolas, say the nth, from the equator (Fig. 23). Let this be denoted by v_n. We measure also the distance, D, from the crystal to the plate. It is clear from the figure that

$$v_n/D = \tan V_n OC = \tan OPN : \text{ and } \sin OPN = n\lambda/c.$$

These relations give the value of c. The value of this method does not lie in its accuracy : the spectrometer can generally do better. But it often happens that some of the spots in the first layer line are absent or very weak. If such spots are searched for on the spectrometer with the object of measuring c they may be overlooked, whereas the whole line on the photographic plate cannot be missed. Thus the observer with the spectrometer may—in the preliminary measurements—use a spot on the second layer under the impression that it is on the first, and so find a value for c which is only half the true value. The importance of the photographic record is all the greater because the ratios of the axes which are recorded in works on crystallography do not in many cases refer to the true unit cell, nor indeed do they claim to do so. The axes chosen on the basis of goniometer readings are parallel to important directions in the crystal, but they may not be simultaneously parallel to the sides of a unit cell.

It is remarkable that so simple a measurement should give at once the distance between two lattice points, a quantity of such importance, and so minute. We can imagine ourselves proceeding to use as axis of rotation two other directions parallel to lines joining a lattice point to neighbouring points, observing as we do so the angles which these directions made with each other. In this way we should determine the constants of the lattice in a very direct manner.

Let us now consider why the spots show a certain arrangement on lines more or less vertical. Take the simple case of an orthorhombic crystal revolving about the c axis, and

consider a spot at N_0 (Fig. 24), due to the plane $(hk0)$. The spacing d of the $(hk0)$ plane is the perpendicular from the origin on the plane

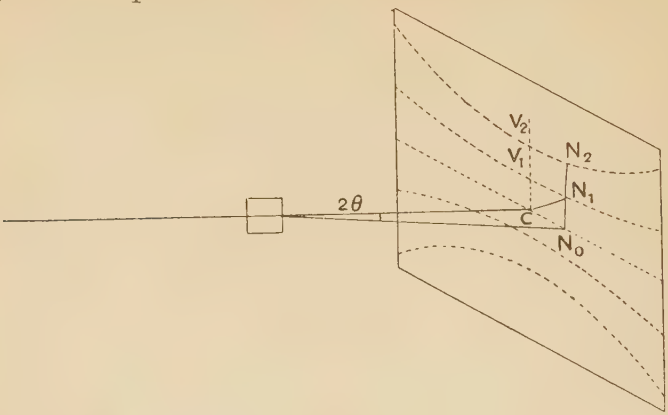


FIG. 24.

$$\frac{hx}{a}+\frac{ky}{b}=1,$$

and is given by

$$\frac{1}{d_{hk0}^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}.$$

The spacing of the $(hk1)$ plane is given by

$$\frac{1}{d_{hk1}^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{1}{c^2}.$$

Now $CN_0/D=\tan 2\theta$. We will at first take points near the centre of the plate, so that θ is small, and therefore $\tan 2\theta$ is nearly equal to $2\sin\theta=\lambda/d_{hk0}$. Similarly

$$CN_1/D=\lambda/d_{hk1}.$$

Hence

$$\begin{aligned}CN_1^2/D^2&=\lambda^2\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{1}{c^2}\right)\\&=\frac{\lambda^2}{d_{hk0}^2}+\frac{\lambda^2}{c^2}\\&=CN_0^2/D^2+v_1^2/D^2 \text{ (see Fig. 23).}\end{aligned}$$

But in the central portion of the plate v_1 is very nearly equal to N_0N_1.

Hence $CN_1^2 = CN_0^2 + N_0N_1^2$, and therefore N_1N_0 is very nearly at right angles to CN_0.

Similarly, the spot N_2 due to the $(hk2)$ plane lies on the second layer at a point above N_1. As we go further the divergences of the spots from a vertical line become greater because the approximations introduce too large an error. It is clear, however, that the spots due to (hkn) planes, where n is a whole number, lie on a curve which near to N nearly coincides with the vertical. The forms of these curves can be obtained by calculation. If, therefore, we know the proper designation of any spot on the equator we can write down the designations of corresponding spots on the layers.

If the crystal is not orthorhombic the curves we have been considering may break up into two sets. Suppose, for example, that the crystal is monoclinic, the c axis being inclined at an angle of 90° to the b axis and at some angle other than 90° to the a axis. Then the spacing of $(hk1)$ is not the same as that of $(hk\bar{1})$. The two corresponding spots lie both on the first layer, and, as a pair, above the $(hk0)$ spot on the equator, but one is closer to the centre than the other. Examples of this may be seen in Fig. 102.

There is yet to be considered one other important method of making the X-ray photograph. It is used when no single crystal of sufficient size can be obtained, and we must be content with a mass of minute crystals oriented irregularly. A monochromatic pencil of rays is passed through a small quantity of the powder, which replaces the single crystal c in Fig. 17. There is now, however, no need to revolve the crystalline mass, for it already contains crystals oriented in all possible ways about the axis. Moreover, there are crystals oriented in all possible ways with respect to the incident rays, and therefore the photograph must be alike in all aspects round the centre : it shows in fact a series of concentric rings, which are circular when a flat plate is used ; on the cylindrical film they take the form of Fig. 20. Each ring gives the spacing of some one set of planes in the crystal. Examples are shown in Figs. 89 and 94. This method, devised independently by Debye and Scherrer, and by Hull, is much

used because the case of a disordered mass of crystal fragments is of frequent occurrence. It gives less direct information than the other methods, but it is applicable when they are not. It will be more fully considered in the last chapter.

Thus we have four principal methods, each having its especial advantage. The well-equipped laboratory can use all four on occasion, since it often happens that a combination of two or more of the methods saves much time and uncertainty. For this purpose it is convenient that the crystal holder should be made to fit all the instruments employed, so that the crystal can be transferred from one instrument to another without disturbing its setting.

Having now considered the measurements that should be made for the purpose of discovering the dimensions of the lattice cell, and the instruments available for making them, we proceed to examine a few actual cases in detail.

First of these comes rocksalt, because it was in point of time the first to be examined, and because so much has depended on the result.

Rocksalt is known to be a cubic crystal, and the unit cell is therefore a cube. Until the X-rays were employed nothing was known either of the dimensions of the cell or of the number of atoms contained in it, or of the pattern according to which the atoms were arranged. Nor, it must be added, was there any exact knowledge of X-ray wave-lengths. Both types of linear dimension, those of the cell and those of the X-ray, were to be inferred from the experiments then begun.

The modern forms of instrument and the technique of their use yield results more simply and quickly than those that were first devised. On this account it is convenient to show how we might now proceed to discover the unknown quantities, supposing ourselves ignorant of the results to be expected, but giving ourselves the benefit of our experience in method.

We mount a minute crystal of rocksalt so that a cube edge is parallel to the axis of rotation of the spectrometer. The photograph so obtained is shown in Fig. 25*a*, Plate III. The drawing in Fig. 26 shows the details of the photograph more

clearly, omitting spots due to the K_β ray, and streaks due to other rays of wave-lengths varying over a considerable range which are generally summed up under the title 'white radiation.' The remaining spots are all due to the K_α ray from the copper target in the X-ray bulb. The distance from the crystal to the screen was 2·37 cm., and the distance corresponding to v_1 in Fig. 23 is 0·675.

Hence $\tan OPN = 0{\cdot}285$ and $OPN = 15° 54'$.

Then $\lambda/OP = \sin OPN = 0{\cdot}274$: so that $OP = a = 3{\cdot}65 \times \lambda$.

The quantity denoted by a is the distance from one point on the lattice to the next point measured parallel to the cube edge.

We next take a similar photograph when the axis of rotation is parallel to the diagonal of the rocksalt cube : a drawing of it is given in Fig. 28. The layer lines are now closer together, and the ratio of the wave-length λ to the distance between two neighbouring points on the lattice along a line parallel to the cube diagonal is found by a similar calculation to be $6{\cdot}32 \times \lambda$. Now $6{\cdot}32/3{\cdot}65 = \sqrt{3}$. This is of course what we should expect if lattice points are arranged on a cubic grating in space. If the distance from point to point parallel to a cube edge is a the distance parallel to a cube diagonal is $a\sqrt{3}$.

The crystal is now mounted with a face diagonal parallel to the axis of rotation ; the corresponding drawing is shown in Fig. 27. The measurement and calculation being made as before we find that the distance from point to point of the lattice in this direction is $2{\cdot}58 \times \lambda$, which is equal to $a/\sqrt{2}$: it is not $a\sqrt{2}$, as we might perhaps have expected. There is, therefore, a lattice point at the middle of the cube face. We know from crystallographic observations that all the cube faces are exactly alike, so that we need not examine, by our X-ray methods, every edge and every diagonal : one of each kind is sufficient. We therefore conclude that lattice points coincide with all the corners of a certain cubic grating and with the centres of the cube faces. We recognise the lattice as one of the three possible forms which can be the

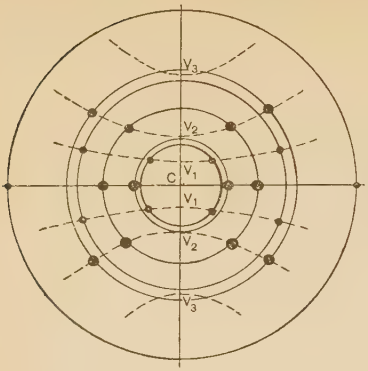


FIG. 26.—Na. Cl. Cube Edge.

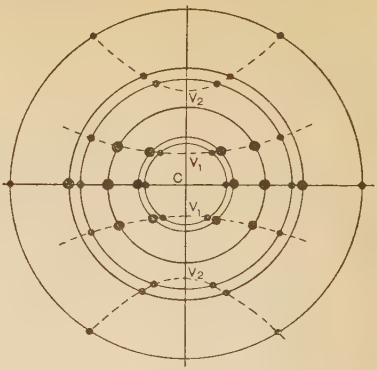


FIG. 27.—Na. Cl. Face diagonal.

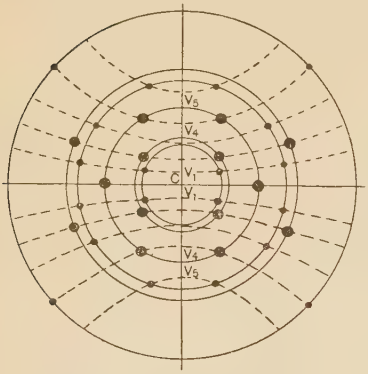


FIG. 28.—Na. Cl. Cube diagonal.

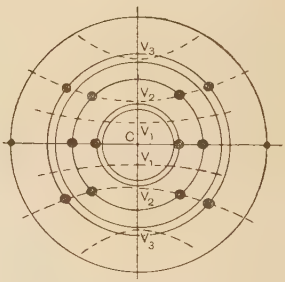


FIG. 29.—K. Cl. Cube Edge.

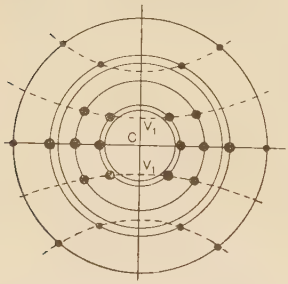


FIG. 30.—K. Cl. Face diagonal.

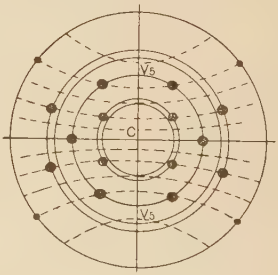


FIG. 31.—K. Cl. Cube diagonal.

In Figs. 26 to 31 the circles are those belonging to various sets of planes as explained in Chapter VI., namely the planes (beginning in the middle and working outwards), (111), (200), (220), (311), (222), (400). The spots are the reflections of the K_α ray from copper. The hyperbolæ or layer lines are shown dotted; the position of these lines alone enters into the present argument.

structural foundation of a cubic crystal. It is the 'face centred cubic' lattice, which was considered at the end of the last chapter.

We now repeat our experiments replacing rocksalt or sodium chloride by sylvine or potassium chloride. The two crystals are known to be isomorphous, and therefore we expect the results to be similar. The results are reproduced in Figs. 25*b*, Plate III, 29, 30, 31 : we proceed to compare them with the corresponding figures for NaCl. If we first of all compare the results when the axis of rotation is parallel to the face diagonal we find that in potassium chloride the distance between two lattice points in this direction is $2{\cdot}87 \times \lambda$. In sodium chloride it was $2{\cdot}58 \times \lambda$, and the ratio of the two is equal to 0·90.

Now we have an independent method of comparing the linear dimensions of the two lattices on the supposition that the crystals are built on the same plan. The density of NaCl is 2·17 and of KCl 1·99. The molecular weights are 58·6 and 74·6. The cell of the cubic grating must contain the same number of molecules in each case, so that if r is the ratio of the linear dimensions NaCl to KCl

$$r^3 = \frac{58{\cdot}5 \times 1{\cdot}99}{74{\cdot}6 \times 2{\cdot}17};$$

whence

$$r = 0{\cdot}896.$$

The agreement between the two numerical results may be taken as proof that our suppositions are so far correct.

But when we compare the other two pairs of drawings we find a difference which seems at first sight to be fundamental. The layer lines for one crystal do not now match those of the other : there seems to be nothing in the KCl picture to match the odd-numbered layer lines of NaCl. If, however, we suppose that for some reason, yet to be found, there are actually spots in the KCl picture to complete the match, but that they are too faint to be seen, then there is as good agreement between the dimensions calculated from the figures, 26, 27 and 28 as from the figures 29, 30 and 31

which we have already examined. Let us compare the second layer lines of the two crystals. The distance of the second layer line in Fig. 29—so called on the supposition that there is a first which is too weak to show—from the equator in KCl is 1·33. In NaCl the equivalent distance is 1·53. From these we can calculate as before the distances between lattice points along the axis of rotation and find them to be $4{\cdot}10 \times \lambda$ and $3{\cdot}65 \times \lambda$ respectively. The ratio of these two quantities is 0·89. In the case of rotation about the cube diagonal the result is similar: the two crystal measurements are in agreement. Such agreements are what we should expect from isomorphous crystals.

We now observe that the first layer line in NaCl in Figs. 26 and 28 is weak relatively to the second, and we search for an explanation of the fact. If we were to imagine that each of the black dots in Fig. 32 represented a mass m_1, and if we were to introduce a different mass, let it be called m_2, at the middle of each vertical line joining two masses m_1, the effect would be exactly such as we observe. For if m_1 were equal to m_2 the centre of that line would be equivalent to a lattice point as far as X-rays are concerned, for we suppose that two atoms of nearly equal atomic weights would have nearly equal effects on the X-rays. The first and third and all odd layer lines would therefore vanish: if m_2 differed appreciably from m_1 these odd lines would appear again and would become stronger and stronger if we gradually reduced m_2 until, when m_2 became zero, the first, second, third layers would fall into a normal scale of decreasing intensity.

The observed effects are explained therefore if in NaCl the black dots of Fig. 32 represent masses m_1, while masses m_2 are placed at the middle point of every vertical line joining two of the m_1 points, as represented by the small empty circle: in KCl m_2 must be equal to m_1. Now this is easily arranged. We suppose that a black dot of Fig. 32 represents a chlorine atom, and each empty circle a sodium atom. The weight of the sodium atom is very different from that of the chlorine. The isomorphous KCl must have the same disposition of atoms except that sodium

is replaced by potassium; and the atomic weights of chlorine and potassium are not far from being equal to each other. Thus the weakness of the odd layers in NaCl and their disappearance in KCl are readily accounted for, and the structure obtained fits all the known facts. The black balls at the corners and the centres of the faces in Fig. 32 may be taken to represent the chlorine atoms, and the rest the sodium, or vice versâ; the two descriptions are equivalent. Most of the alkali halides possess the same structure.

As yet we have not obtained any absolute measurements either of spacings or wave lengths; our determinations relate only to ratios. If, however, we assume the structure of Fig. 32 to be correct, we can use it in conjunction with other data to find what we want.

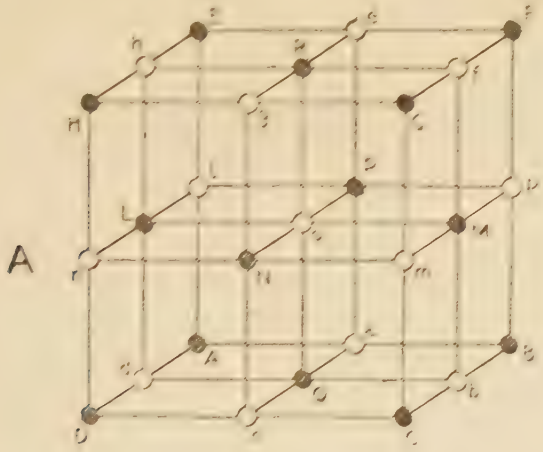


FIG. 32.

The specific gravity of NaCl is 2·17. The cube of Fig. 32 has therefore a mass $2{\cdot}17 \times a^3$, where a is the length of the edge. The cube contains four atoms of sodium, and, of course, an equal number of atoms of chlorine. For it is to be remembered that the corners of the cube coincide with the centres of the corner spheres, and therefore only one eighth of each of these spheres is within the cube. Similarly, only one half of each of the spheres at the face centres is

contained within the cube. Thus the effective number of sodium atoms in the cube is

$$8 \times 1/8 + 6 \times 1/2 = 4.$$

The molecular weight of the NaCl molecule is 58·5, and the mass of the hydrogen atom is $1{\cdot}64 \times 10^{-24}$.

Thus we have

$$a^3 \times 2{\cdot}17 = 4 \times 58{\cdot}5 \times 1{\cdot}64 \times 10^{-24},$$

whence $$a = 5{\cdot}62 \times 10^{-8},$$ or 5·62 A.U.

Once the dimensions of the rocksalt lattice are known it is an easy matter to calculate the wave-length λ that has been used in the experiments; or any other wave-length provided its deflection by one of the rocksalt planes has been observed. So also, knowing the absolute values of the wave-lengths we employ, we can use them to find the spacings of any crystal planes whatsoever, so long as a reflection can be observed. The wave-length of the radiation from copper, which was used in taking the photographs, is thus calculated to be 1·54 A.U.

The determination of the structure of rocksalt, the first crystal structure to be measured, was the starting point of all measurements of wave-lengths and spacings. Rocksalt is not well suited, however, for very accurate comparisons. The crystal is generally ill-made, consisting of a mass of smaller crystals imperfectly aligned with each other. Calcite is much better formed, and is now in general use as the standard of measurement: diamond might perhaps be better still. Comparison in X-ray spectrometry has now reached such a pitch of accuracy that it is found necessary to assume an ideal grating constant. Siegbahn in his treatise on *The Spectroscopy of X-rays* assumes a value for the (111) spacing of calcite which is expressed by a seven figure logarithm: he puts $\log 2d = 0{\cdot}7823347$. This gives $d = 3{\cdot}029038$. By a calculation similar to that carried out above for the case of rocksalt Siegbahn finds $d = 3{\cdot}0283$ with an accuracy of about 1 in 1500. Thus the accuracy of Siegbahn's assumed figure is artificial, but it is necessary

because comparisons can be made to an accuracy at least ten times as high as that of the calculation, and observers must have a means of bringing their observations to a common if ideal standard.

Yet one more observation should be made. We have supposed that the alternate masses along the cube edge of the rocksalt crystal are sodium and chlorine. There was, of course, a certain assumption in this: conceivably the alternate masses might have been respectively p sodiums with q chlorines, and q sodiums with p chlorines, where p and q are integers. This assumption was rejected originally because there seemed to be no reason for such a complicated arrangement. And a justification soon appeared in the fact that the wave-lengths found on the simple hypothesis were in agreement with the deductions from quantum theory. The quantum energies of the rays issuing from the X-ray bulb corresponded to the energies imparted to the electrons which excited them.

Having gone thus far with our analysis of structure we may well pause to consider what connection may be found between the design of the structure, its component elements and its properties as a whole. The peculiar relation of the chlorine and sodium atoms to one another were a matter of some surprise at the time of their discovery. The molecule seems to have disappeared. Each atom of the one kind is not paired with one atom of the other: it is similarly related to the six atoms of the other kind which are its immediate neighbours, and no one of the six can be considered as its special partner. If we adopt the common view of what happens when sodium and chlorine atoms are assembled together we must consider each sodium atom to be positively charged, having parted with one electron, and each chlorine atom to be negatively charged, having taken to itself an extra electron. The positive atom will naturally gather round itself negative atoms, and *vice versâ*: the structure we have found is the result. Each positive has six negatives as nearest neighbours; each negative, six positives. In this way the design of the crystal can be partially explained.

We must not say 'fully' explained, because, for example, we do not know why the atoms are so spaced that their centres are 2·81 A.U. apart. It would be very unsatisfactory to say that they are spheres which are brought into contact by electrostatic attraction: for we do not know what contact means, and would rather hope to discover an explanation of contact than to use it in explanation. We may suppose the existence of a force of repulsion which rapidly increases as the atoms approach each other. Born showed that if there were such a force, proportional to the inverse ninth power, volume elasticity and other properties could be conveniently accounted for. But all properties are not explained in this way: some, such as rigidity, must be due in part to forces other than central. Most of the alkali halides are isomorphous with rocksalt, but rubidium fluoride is not; nor are the chloride, bromide, iodide of caesium. These four possess a body centred structure, the unit cell having an atom of the one kind at the centre of the cube and atoms of the other kind at the corners. Consequently, the principle that each atom will gather round it a certain constant number of the other kind gives only a partial explanation, even though it is obviously the dominant principle in the cases we have been considering.

It is known from other sources that the atoms of sodium and of chlorine, when they have lost and gained one electron respectively, are similar to the rare gases neon and argon in many of their properties. Were it not for their electrostatic attraction their tendencies to combine with other atoms would be small. Their surrounding fields of force are highly symmetrical. It is not surprising therefore that the rocksalt structure shows the highest possible symmetry. It has, indeed, been supposed that sylvine is less symmetrical than rocksalt on the ground that under certain circumstances unsymmetrical etch figures can be formed upon it. It has lately been shown, however, that the effect is due to impurity in the etching liquid, and this removes a difficulty, since such a lack of symmetry could not be reconciled with the X-ray results. All these substances are truly isomor-

phous, and show the highest possible symmetry. The crystallographer places them in Class 32.

The solution of the rocksalt problem makes us free of the crystal world : we have shown that such problems are soluble and we have calibrated our instruments. It is true that we are yet far from being able to obtain the complete solution in every case : crystals in the vast majority are much more complex than rocksalt. But we can always do something, and we may hope, by making many attempts and carrying each of them as far forward as our present powers of analysis permit, to strengthen our technique and increase our knowledge of the structural laws so as to approach continually nearer to success in every case.

CHAPTER III

SIMPLE INORGANIC CRYSTALS

As we survey the field opened out by the experimental determinations of the last chapter we find that we must decide the directions in which we are to make our first advances. The choice is simplified by the observation that there appear to be certain distinct types of structure. Rocksalt and its isomorphs are examples of the "ionic" type in which there are positive and negative components, and the forces that hold them together are electrostatic, at least in part. Many inorganic substances belong to this class.

In a second type of structure there is no ionic separation; the atoms are tied together by such bonds as join atom to atom in the chemical molecule and, since these bonds hold the whole structure together, the crystal is one great molecule. The most striking example of this type is the diamond.

In a third type, represented with great frequency in the organic world, the molecule or group of atoms, which as a whole is unchanged by its entrance into the crystal structure, is linked up to its neighbours by ties which are generally weak, the atoms within the molecule or group being held together with far greater strength. Naphthalene may be taken as an example.

Diamond is not only interesting as a type. The carbon atom is of such importance, in organic chemistry particularly, that its crystalline state invites consideration with the greatest care. As a crystal diamond has most remarkable properties, and it is of course a matter of great interest to connect its properties with its structure. It is a very perfect crystal, so that great precision is obtainable in the analysis, and this also is attractive. We may follow the same procedure as in the case of rocksalt, mounting a diamond on

the axis of rotation of the spectrometer and obtaining the three photographs when the axis of rotation coincides respectively with the cube edge, the cube diagonal, and the face diagonal. It then appears that the lattice is of the face-centred cube variety as in the case of rocksalt. Calculation shows further that two carbon atoms are associated with each point on the lattice, and it remains to find their disposition more exactly, for which purpose it is necessary to take account of the intensities of reflection by the different crystal planes.

We will, however, adopt a different method which will allow us to illustrate the use of the ionisation spectrometer.

We know that the crystal is cubic : let a be the length of the edge of the cubic cell, which, it should be observed, need not be and in fact is not the unit cell. The density of diamond is 3·51. The mass of the carbon atom is $12 \times 1{\cdot}64 \times 10^{-24}$. There must be a whole number of carbon atoms in the cell, say n.

Then $$a^3 \times 3{\cdot}51 = n \times 12 \times 1{\cdot}64 \times 10^{-24},$$

whence $$a = 1{\cdot}776 \times n^{\frac{1}{3}} \text{ A.U.}$$

The number n is almost certainly small ; most probably it is either 1, 2, 4 or 8. There seems to be no reason why it should be such an odd number as 3, 5, 6 or 7. At any rate we try the simpler numbers first.

If $n = 1$, $a = 1{\cdot}776$.
,, $n = 2$, $a = 2{\cdot}238$.
,, $n = 4$, $a = 2{\cdot}820$.
,, $n = 8$, $a = 3{\cdot}552$.

We set up the diamond on the ionisation spectrometer and search for a reflection from the cube face. It is true that the cube face is not likely to be present on the diamond ; but if the diamond has a tetrahedral form the proper orientation can be made without much difficulty, and indeed the spectrometer itself can be used for the purpose. The X-ray bulb has, let us say, a molybdenum target : the wave-length of the α ray is 0·712. A reflection is found from this cube face

when the glancing angle is 23° 40′, and at no smaller angle. This gives, since $\lambda = 2d \sin \theta$, $d = 0{\cdot}888$.

If we now compare this value with the possible values of a given above we observe that it is exactly half the value of a, supposing $n = 1$, or one-quarter the value of a if $n = 8$. It is incommensurable with the values of a, supposing $n = 2$ or 4 (or 3, or 5, or 6, or 7). The interpretation is that either there is one atom in the cell, and the reflection we have observed is the second order of reflection from (100), or as we say more conveniently, the reflection from (200) : or else there are eight atoms in the cell and we have been observing the reflection from (400). The absence of the lower orders is to be ascribed to interleaving, and we shall have to make use of this fact when we consider the details of the arrangement in the cell.

We now consider the reflections from the (110) face. We find a reflection at 16° 20′, whence d is in this case equal to 1·26 nearly. The reflection from the (111) face occurs at 10° 0′, whence the corresponding $d = 2{\cdot}05$. This last value shows at once that $n = 1$ is impossible, since the (111) spacing of a cube is at most equal to $a/\sqrt{3}$, where a is the edge of the cube (p. 24). But if $n = 8$ there is agreement, since

$$2{\cdot}05 \times \sqrt{3} = 3{\cdot}551.$$

We are now almost certain that there are eight atoms of carbon in a cell of which the edge has the length 3·552.

Now if the corners of the cell were the only lattice points, as in the simple cubic cell, or corners and cube-centre as in the body centred cubic cell, the value of the (110) spacing would be $3{\cdot}552/\sqrt{2} = 2{\cdot}52$: twice the experimental value. It will not help us, therefore, to suppose that the cell belongs to either of these types. But our results will fit the supposition that the lattice is face centred cubic, as in the rocksalt case, since in that case the (110) planes are interleaved : there is no (110) reflection, the first to occur is the (220). We thus infer that the lattice, which we know to be cubic since diamond is a cubic crystal, is of the face-centred cubic type.

There are four lattice points, as we have seen before, in a

face-centred cubic cell. As there are eight atoms in the cell there are two atoms to each point. We have still to place them relatively to each other. In order to appreciate what is implied in this operation let us suppose one atom to be placed at each point of the lattice, that is to say at the corners and face centres of Fig. 33. To every such atom a

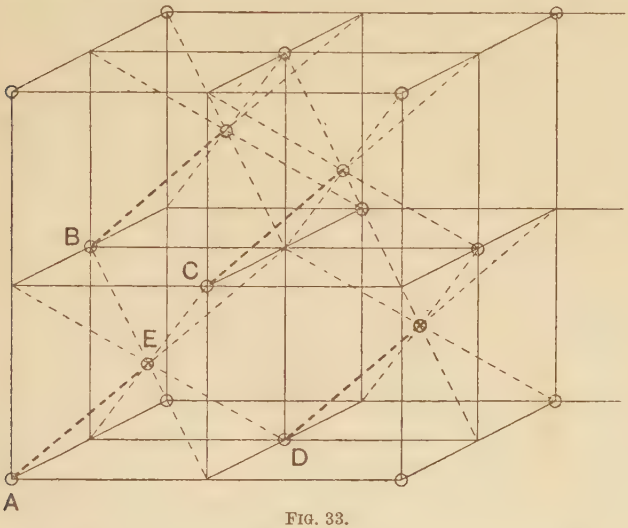


Fig. 33.

second atom is to be related, and the relation must be the same in each case : the straight line joining the pair must have the same length and lie in the same direction. That is because each lattice point must represent the same thing : the circumstances about each point must always be the same. We may, therefore, picture the second set of atoms as derived from the first by means of a translation of the lattice in some direction and to some distance yet to be found. We are here assuming that the carbon atom may be considered spherical. This is not true, but it is very nearly so : and for our present purpose the assumption is justifiable. The observed X-ray effects must be sufficient to determine the amount of translation, and indeed we need only appeal to one of them, viz. the absence of the (200) reflection. The second lattice must be moved by an amount $a/4$ in each of the three

principal directions so as to interleave at the same time (200), (020) and (002). That is to say, the direction of moving is the cube diagonal, and the amount is equal to one-quarter of the length of the same diagonal. The movement is indicated by the thick dotted lines in the figure ; it could equally well have been indicated by thickening any one of three other differently oriented sets of dotted lines. The positions of all the carbon atoms have now been determined.

The structure now obtained and represented in Fig. 33 can be represented also as in Fig. 34, in which the black balls

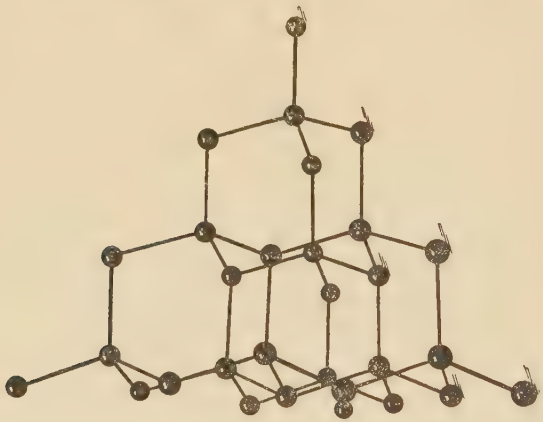


Fig. 34.

represent the carbon atoms. There is no difference between the arrangements in Figs. 33 and 34, except that in the latter case the rectangular framework has been omitted. It is clear that we have arrived at a construction which can now be described very simply ; its main feature is that every carbon atom is at the centre of gravity of four others. As a matter of fact this feature forms a complete definition of the structure if the latter is to be cubic. There is no other structure of which the same can be said, except that which is based on hexagonal close packing (see p. 152) just as diamond is based on cubic close packing.

Reflections from all planes should support the conclusion

thus reached ; but we will consider only one such confirmation. It is a striking fact that the second order reflection from the (111) plane of diamond is exceedingly small : this is readily to be seen in Fig. 35, which shows the ' spec-

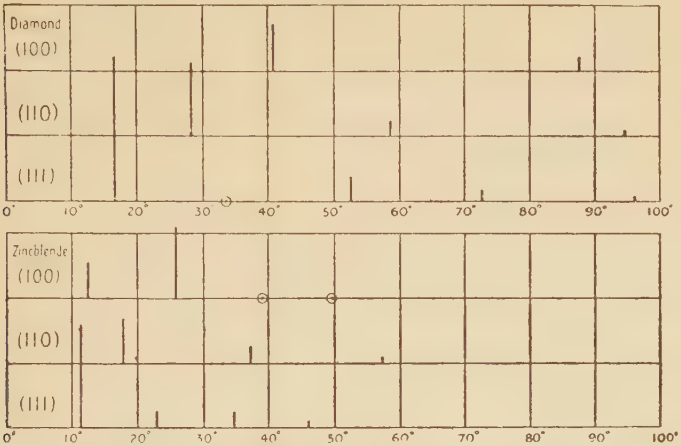


FIG. 35.—The upright lines show the reflections to various orders by the cube face, and two other important sections of diamond: in other words the top line shows a good reflection by (400) and a weak one by (800): the third line indicates a strong (111) reflection, no appreciable (222), and weaker reflections by (333), (444) and (555).

trum ' of reflection in this plane as measured by the ionisation spectrometer. Now, if we take the model of Fig. 34, and consider the succession of planes parallel to the tetrahedral face which rests on the table, we observe that these planes are spaced at intervals of $d/4$ and $3d/4$, where d is the spacing measured by the spectrometer, the true spacing of the (111) set of planes. This follows from the fact that the centre of gravity of a tetrahedron is at a distance from the base equal to one quarter of its height. The succession is represented in Fig. 36. When such a set of planes is giving a second order reflection the difference in phase between the reflections from A_1 and A_2 is 2λ, and therefore the difference in phase of A_1 and B_1 is $\lambda/2$. Thus the B reflections are exactly opposite in phase

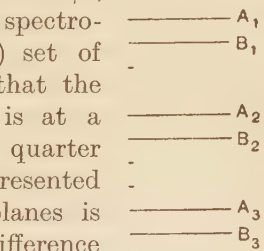


FIG. 36.

to the *A* reflections, and the set of planes as a whole does not reflect at all.

Thus the assumption of a spherical (or indeed a cubic) form for the atom makes the (222) reflection disappear entirely. Experiment shows it to be very small. If the atom is supposed to have a tetrahedral form in conformity with its tetrahedral surroundings, the (222) reflection does not disappear : the *A* and *B* planes of Fig. 36 are not identical, because they represent tetrahedra pointing opposite ways (Fig. 34). The (200) reflection still vanishes, however, because this set of planes exactly bisects all the tetrahedra, viz. those of both orientations.

The almost total disappearance of the (222) reflection is indeed sufficient evidence of the structure. If at the outset we had assumed total disappearance in the case of four tetrahedral faces, we should have concluded that each carbon atom in the structure was at the centre of gravity of four others, and the description of structure would have been complete. We have taken a longer but perhaps more natural path leading to the same result.

The structure is in obvious accord with some of the well-known properties of diamond. When the structure of any crystal is first determined it is natural to look at once for correlations between structure and properties. Indeed, the whole of this investigation is carried on in the hope that such relationships will be discovered, and that the properties will thus be better understood.

The quadrivalency of carbon could not be more clearly illustrated : the structure is based upon nothing else. In the next place we remark an obvious arrangement of the carbon atoms in rings of six, which recalls at once the fact that the carbon hexagon found in its simplest form in benzene is the basic structure of the aromatic division of organic substances. The diamond is, of course, remarkable for its hardness : it is natural to suggest the perfection of the arrangement as an explanation. Each atom is bound with equal strength to four symmetrically placed neighbours, and the bonds seem to be of the kind that join atom to atom

in the molecule. The diamond is able to scratch any other substance because in no substance are the atoms held more firmly in their places. These are some of the most obvious correlations.

There is a second crystalline form of carbon, viz. graphite. The determination of structure is much more difficult than in the case of diamond, but it has been completed independently by Hassel and Mark and by Bernal. The two sets of results are in agreement. The drawing in Fig. 37 is due

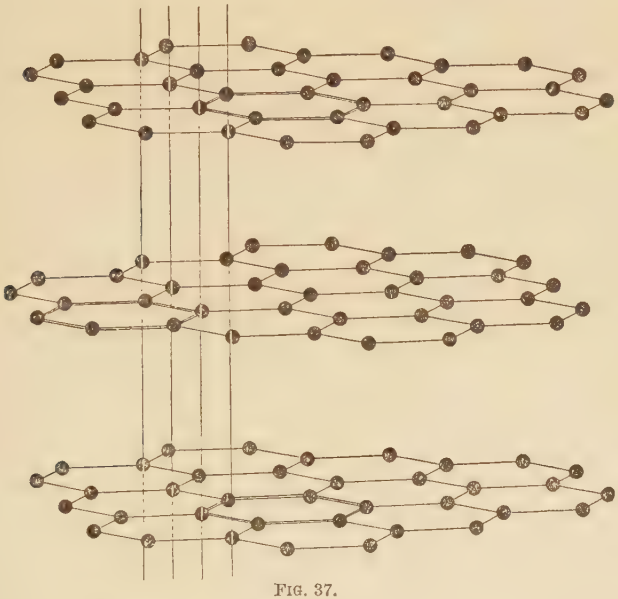


FIG. 37.

to Bernal. We shall not describe the methods of solution, but accept the conclusions. The crystal is hexagonal; it consists of separate sheets, in each of which there is a similar hexagonal network. In each sheet the distance between any two carbon atoms is 1·42 A.U., which is rather less than the distance between any two atoms in diamond. The sheets are separated from one another by distances unexpectedly great, no less than 3·41 A.U. This very remarkable structure possesses just those differences from diamond which

make it easy to explain the great differences in the properties of two forms of carbon crystal. Graphite is a flaky substance; when beaten in a mortar it breaks up continually into thinner and thinner flakes, but it does not become a powder. This is readily explained as due to a difference in strength of the bonds between two neighbouring carbon atoms in the same layer and in adjacent layers respectively. Two neighbours in any one layer are drawn together more closely than two carbon atoms in diamond. But the great distance between layer and layer is naturally associated with weakness in their mutual attraction.

It is just this peculiarity that makes graphite so perfect a lubricant. One layer can slide freely over another, and at the same time each layer is a well-knit assemblage and is not easily broken up. The bonds are strong in two dimensions and weak in the third, which is exactly what is wanted. The same explanation holds as we shall see later in the case of oils, fats and greases.

For these reasons also it is difficult to find a good graphite crystal : the graphite specimen resembles a pack of slippery cards thrown in a heap upon a table. If they ever were fitted to each other correctly it has been easy to displace them ; and if they have grown into their present form it is easy to understand that the flakes might not grow correctly together.

We have no simple explanation as yet of the greatness of the distance from layer to layer. It is a distance which can be measured with great exactness, and no variation with circumstances has yet been found. There does not seem to be sufficient reason for supposing that the distance is anything else than a quantity inherent in the carbon atom : associated in some way with a weak connection, just as in diamond and in the single graphite flake, the closer approach goes with a connection of greater strength.

The structures of diamond and rocksalt are so simple and so symmetrical that a very few observations of their X-ray reflections have been sufficient to determine them completely. There is no question of any approximations in fixing the

positions of the atoms. The reason is that the X-ray measurements have been merely arbiters between a limited number of possible solutions : and the very roughest observations were enough for an absolute decision. Once that decision was made the rest was a matter of geometry, requiring no physical observations and therefore entirely free of error. Not many crystals can be dealt with in this way. As a matter of fact the diamond structure we have deduced was suggested long ago by Nernst. The X-rays have been able to go a step further than suggestion, and to show that this is the only possible structure.

The question then naturally arises, can any use be made of the many possible observations of reflection by different planes in the crystal ? The answer is that, so far as such observations depend on structure only, we cannot expect any new information. If they did not agree with calculations we should be obliged to conclude that we were in error from the beginning ; that, in fact, the crystallographers' determinations of the symmetry of rocksalt and diamond were mistaken. Nothing of this kind has been found.

But as regards the relative intensities of the different reflections it is a different matter. Their magnitude must depend on many factors. How, for example, does the contribution of an atom depend upon its mass or atomic number, how upon its extension in space ? Is it the same in all directions and for all orientations to the incident rays, and if not what are the laws of variation ? How does the observed intensity depend on imperfections in crystal structure, and on temperature ? The answers to these questions are, as a whole, exceedingly difficult, and it is fortunate that in regard to the simpler crystals at least they are not required in the determination of structure. The usefulness of intensity measurements is very great in other directions, however, as, for example, in finding replies to the questions just asked ; and all the more so because structure has been determined without their aid, and therefore without possibility of error.

When we come to consider more complicated crystals we

are obliged to base some of our reasoning as to atomic position on considerations of intensity, because the possible choices are no longer definite and limited in number. Symmetry considerations leave possibilities that the solutions may lie anywhere within given ranges, and the intensity measurements must complete the determination as well as they can.

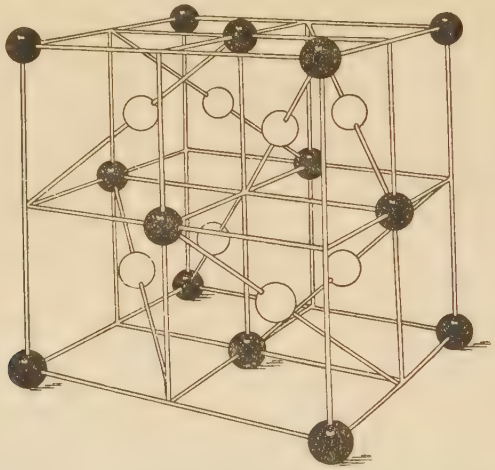


FIG. 37 (*a*).—A perspective view of a model of the calcium fluoride structure.

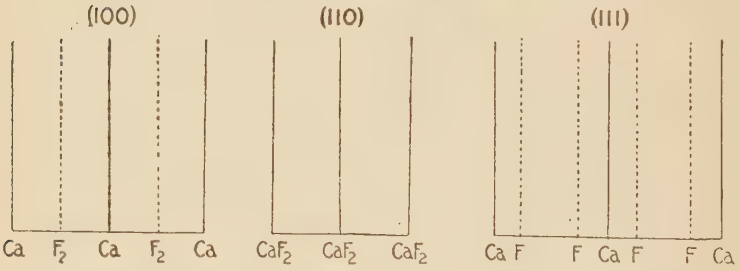


FIG. 37 (*b*).

We may perhaps smooth off the transition from the one kind of crystal to the other by considering the structures of calcium fluoride, which is of the ionic type like rocksalt, and of zinc blende, which in structure resembles diamond.

It is not necessary for our present purpose to consider the solutions in the detailed manner of the two previous cases.

Calcium fluoride (CaF_2) is a cubic crystal of the highest possible symmetry. The measurements show that the lattice is of the face-centred type. The length of the edge of the cube in Fig. 37*a* is 5·5 A.U., and the cube contains the substance of four molecules. One molecule is therefore associated with each corner and each face centre of the cube : let us suppose that a calcium atom is placed at each of these points. We have now eight fluorine atoms to put in their places. The symmetry is so perfect that there can be no question as to where they must go : they must be put at the centres of the eight small cubes with which the large cube is divided. We arrive at the structure of the figure. No matter what intensities we may observe in the X-ray reflections not the smallest departure from this structure can be considered.

Now, when we examine the reflections from the cube face we find of course that there is no reflection of the first order ; this is to be expected as we have a face-centred cube. But there is no appreciable second order reflection either. An explanation is at once forthcoming ; planes parallel to any cube face contain alternately calcium and fluorine atoms, and the number of electrons associated with the atoms in unit area must be nearly the same for the two planes. Thus the reflecting powers of the two kinds of planes must be nearly equal, the (200) reflection disappears and the (400) is the first to occur. In the same way it can be shown that, as in diamond, the (222) reflection should be very small : and that also is found to be the case. But it is very interesting to find that the reflections from (600) and (10,00) are far from vanishing. If under all circumstances one calcium atom were equivalent to two fluorines these reflections should not appear. As they do, we must conclude that at the higher angles of reflection the balance is not so good as at the smaller angles. These intensity variations depend on atomic configurations, and their presence does not affect the determination of crystal structure in any way whatever ; rather, they offer a means of investigating the structures and behaviour of the atoms themselves.

The structure of zinc blende (ZnS) resembles closely that of diamond, and the comparison of the intensities of the reflections due to the two crystals will give us a second convenient example of the effects due to the presence of more than one kind of atom. In this case also the X-rays

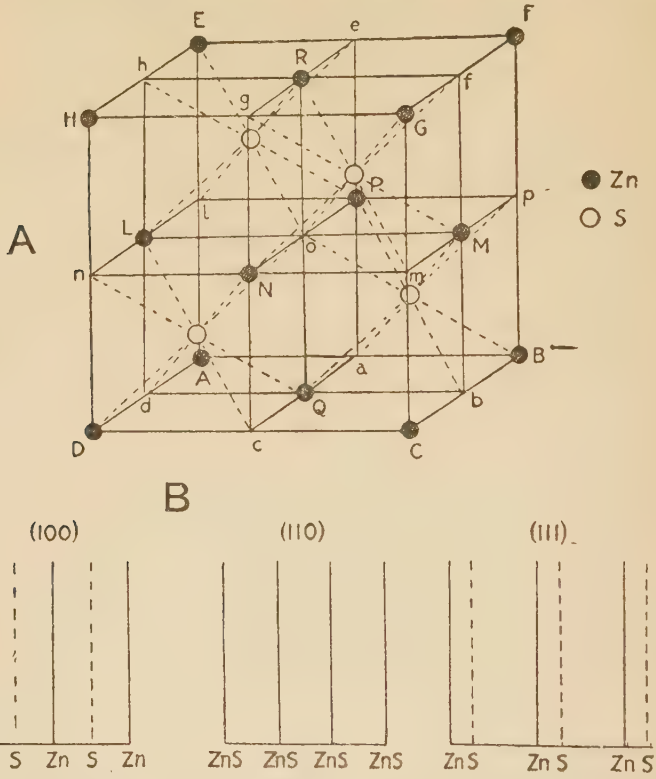


FIG. 38.

have been called upon to do no more than indicate which of various possible structures is the right one. The lattice is again the face centred cube, and there are four molecules in the cubic cell. If we first place a zinc atom at each cube corner and face-centre, that is to say at each point on the lattice, we have then to place the corresponding sulphur atoms. The face-centred cube of zinc atoms has the highest possible symmetry, and the system of sulphur atoms must be

added to the zinc system without disturbing the symmetry, except in one particular : the crystal has polar properties along each of the cube diagonals. There is only one way of doing this : as in the diamond we must displace the sulphur lattice, supposing it to be at first in coincidence with the zinc lattice, parallel to any one of the cube diagonals by an amount equal to one-quarter of the diagonal of the large cube. Thus the structure is the same as that of the diamond except that half the atoms are sulphur and half are zinc. Every zinc atom is placed at the centre of a regular tetrahedron of four sulphur atoms, and *vice versâ* (Fig. 38). The crystal becomes polar because of the manner of the arrangement of the zincs and sulphurs along each diagonal ; but all other elements of symmetry remain.

It is now interesting to consider the intensities of reflection by the different planes. The reflection from (200) is abnormally small, because this set of planes consists of zinc and sulphur planes alternately, and the (200) spacing is the distance from zinc plane to zinc plane, or sulphur to sulphur. In diamond the planes were all carbon planes and the interleaving was complete, so that there was no (200) reflection. Here the planes are not equal, so that there actually is a (200) reflection, but it is small. Again, the (222) reflection does not become insignificant as in diamond, but it is found to be quite small. These peculiar intensity effects are due to the difference between the zinc and the sulphur atoms themselves and are available for investigation into that difference. The structure is perfectly known and forms a sure ground for further experiment. The case of zincblende illustrates a peculiar limitation of the X-ray methods. Exactly the same reflections are obtained from a (111) set of planes as from a ($\bar{1}\bar{1}\bar{1}$) ; or, in other words, from a face cut at one end of a cube diagonal as from a face cut at the other end. Polarity escapes direct observation. Nevertheless the polarity of zincblende is clearly to be inferred from the result obtained.

Let us now consider cases in which the structure is not determined by such simple considerations. Iron pyrites (FeS_2) is a very good example.

The crystal is cubic, but its symmetry is not quite of so high an order as that of rocksalt or diamond. Its very appearance shows that ; for there are striations on the faces which are related to one another in the curious manner shown in Fig. 39*a*. Clearly the cube faces are planes of

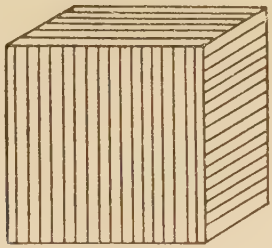


FIG. 39 (*a*).

symmetry, but not the (110) planes. In this respect alone the crystal symmetry falls short of the maximum. It still possesses the trigonal symmetry round any cube diagonal ; and also it is centro-symmetrical, it is not polar like zinc-blende.

The X-ray analysis shows at once that the edge of the unit cell is 5·4 A.U., and, knowing the molecular weight of FeS_2 and the density of the mineral we readily find that there are four molecules in the cell. So far, again, the intensities of the X-ray reflections have not been taken into account at all. Even the measurements of the spacings may be ignored as soon as a rough determination of them has shown us that the number of molecules in the cubic cell is four, because we are then in a position to proceed to certain determinations of the positions of the molecules.

Let us suppose that molecules are placed at the corners of the cell ; any one of these molecules can be made to coincide with any other by translation parallel to the cube edge. They are in fact similar in all respects : if they have special orientation, and we shall see presently that they must have, then the orientation must be the same for all of them. The collection forms a simple cubic lattice. There are three other molecules belonging to the cell. Each of these is

repeated in space as often and as regularly as the first, and by such repetition also forms a simple cubic lattice, which is similar in dimensions and orientation to the first. The four molecules in the cell need not be, and in fact are not alike in all respects. The structure is not of the face-centred cube variety.

Consider now the trigonal axes; there are to be four, parallel to the four cube diagonals respectively. If, by rotation through successive steps of 120° round one of these axes, the crystal is brought to coincidence with itself, there must be one group which is individually brought to self-coincidence at each step, while of the other three the first must take the second's place, the second take the third's and the

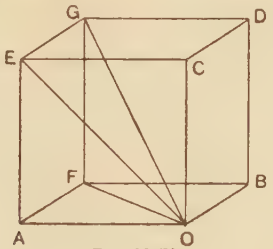


FIG. 39 (*b*).

third take the first's. Suppose, for example, that *OG* (Fig. 39*b*) is a trigonal axis: then, in the rotation of 120° about *OG*, the molecule at *O* must become self-coincident after the rotation, the molecule at *A* takes the place of the molecule at *C*, *C* goes to *B* and *B* to *A*, and so on. But this is only possible if the molecule at *O*, and therefore all molecules on the same cubic lattice as *O*, has a trigonal axis parallel to *OG*. In this way the lattice to which *O*, *G*, *A*, *B*, *C*, . . . belong is brought to self-coincidence. As for the other three groups they must be so disposed that they take each other's places as already described. We shall see later that this is easily arranged for. Thus the one iron and the two sulphur atoms which are associated with *O* must be spaced along the diagonal through *G*. Moreover, as the crystal is not polar, the iron atom must lie symmetrically between the two sulphurs, as otherwise the crystal would show differences at the two ends of a trigonal axis, like zincblende.

All four sets of molecules must be alike in structure, since they are capable of taking each other's places during trigonal rotation. So every molecule is arranged in the symmetrical succession S—Fe—S. Moreover, in order that the four trigonal axes may be provided, each of the four molecules must be disposed with its axis parallel to one of the cube diagonals, as the molecule at *O* is disposed with respect to *OG*.

Each molecule has a centre, and if we can now place the centres the relative positions and orientations of the molecules will be completely determined. There is only one possible solution to this problem : the centres of the iron atoms must lie at the corners and face centres of a face-centred cube. Under such circumstances every molecule is similarly related to its surroundings, and there is no other arrangement for which this is true. The outcome of the argument so far is represented in Fig. 40, where the white

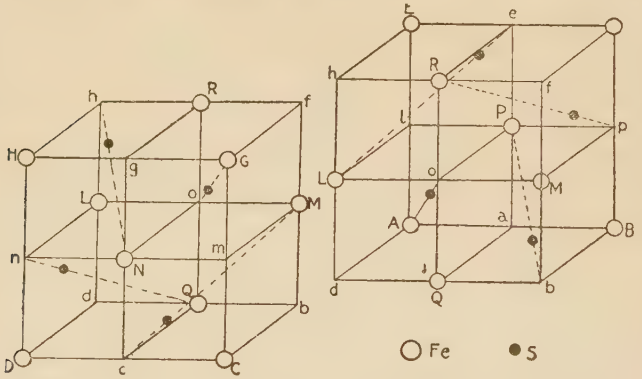


FIG. 40.—The two halves of the iron pyrites cell are shown separately, so as to avoid confusion of lines and letters.

balls represent iron atoms and the black sulphur. The figure is drawn in two parts so that the details may be seen more clearly. A study of the figure will now show how one lattice takes the place of another during trigonal rotation. In the rotation about *AG*, for example, one of the four molecules that belongs to the cube lies on the axis, the lines *Nh*, *Rp*, *Mc* rotate into each other's places, and each of these lines carries, and is the axis of, one of the other three molecules of

the cell. If we would examine the rotation about another diagonal direction such as Nh we find it convenient to shift our origin to N, making it the corner of that cubic part of the lattice which we now consider.

Up to this point we have based our arguments on questions of crystal symmetry and the X-ray determination that there are four molecules in the cell. In making that determination the roughest X-ray measurements were sufficient, because the X-rays were only called on to decide between certain widely differing possibilities. We have not used our power of making very accurate measurements of the cell dimensions : if we desire to do so we may, by means of such measurements, determine accurately the specific gravity of the pure material. It often happens that the customary methods of determining densities do not give results that are free from ambiguity, because the natural material may contain minute intrusions and cavities, whereas the X-ray observations are independent of such disturbing factors. But we do not need accurate values of the specific gravity in this type of problem. Neither have we so far made use of the easily observed differences of intensity of reflection by various sets of planes. We must now, however, try to employ intensity differences if we are to finish our problem, because there is one point in the structure which is yet to be settled, and this cannot be determined by symmetry considerations. We have not found the distance between the centres of an iron atom and its sulphur neighbour : everything else has been done by our first simple analysis, but this is outside its range. We must call the intensity measurements to our aid.

The diagram in Fig. 41 shows the results of measurements by the ionisation spectrometer of the reflection from the (100) (110) and (111) sets of planes. The heights of the thick black lines show roughly the relative intensities of the reflections observed. Let us consider in the first place the reflections from the cube face. If our reflection planes consisted only of the cube faces themselves, the spacing being 5·43, and if we used the α rays of Rh for which $\lambda = 0{\cdot}614$, we should find reflections at values of θ for which $\sin\theta = n\lambda/2d = n \times 0{\cdot}0564$

i.e. 3° 14′, 6° 29′, 9° 44′, 13° 2′, ... The angles at which the ionisation chamber would be set to receive these deflections would be twice as great, viz. 6° 28′, 12° 58′, 19° 28′, 26° 4′, and so on. Also, we should expect that the reflections would gradually decrease in intensity from the lower to the higher orders. Comparing these with the observed results we see at once that all the odd orders are absent. For this there is an immediate explanation. The arrangement of the atoms in consecutive planes is sketched in the first of the three

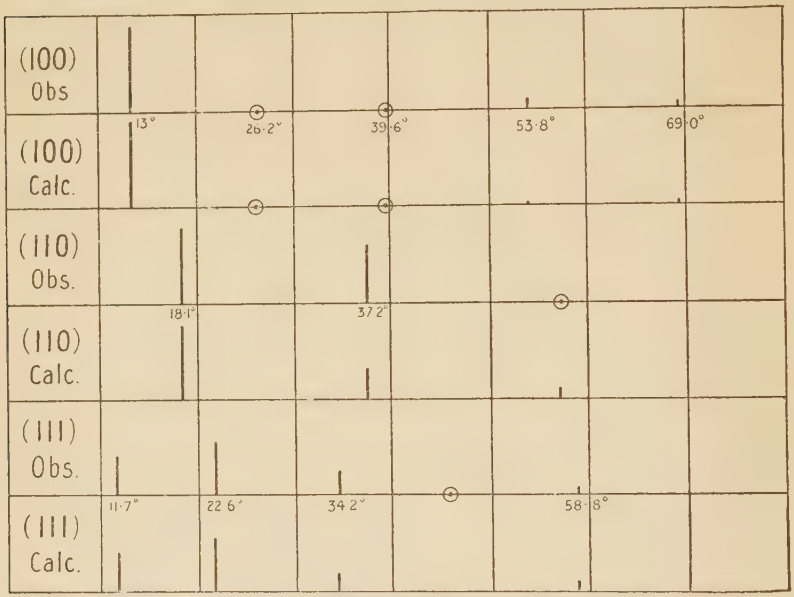


FIG. 41.—Diagram of the intensities of reflection by various sets of planes in iron pyrites. For example the first line shows a strong second order or (200), extremely small reflections by (400) at 26·2° and (600) at 39·6°; weak reflections by (800) and (10,00). There are no odd order reflections at all, as explained in the text.

drawings of Fig. 42. It is clear that the 5·43 spacing is halved. This is, of course, usual in a face-centred cubic grating, and the iron atoms have the positions represented by that grating; but we draw the figure in order to show that the sulphurs also have been so arranged that their projections on the plane of the paper are symmetrical about each iron plane.

We now proceed further so as to bring in the effects of the relative positions of the sulphur and iron atoms. We observe that the intensities of the fourth and sixth orders are very small. The weight of one iron atom is nearly equal to the weight of two sulphur atoms, so that if we can get the iron into opposition to the sulphurs the corresponding reflection will nearly disappear. Suppose that in Fig. 43, which shows separately a part of Fig. 40, AS is one-quarter of AO, and therefore one eighth of AG. Then, in the fourth order, the

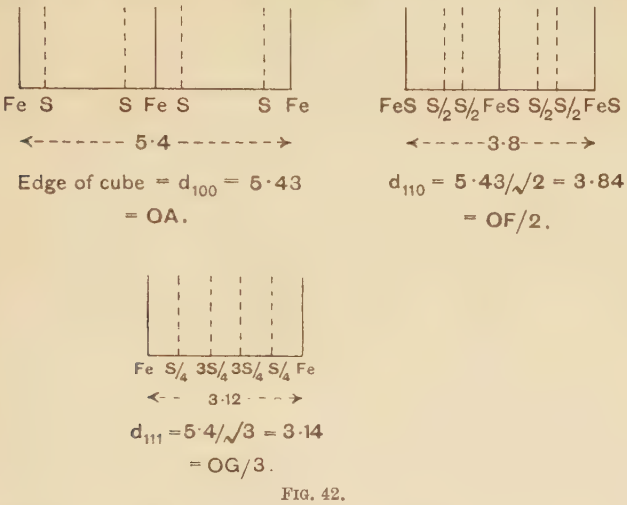


FIG. 42.

difference of phase of (100) planes containing A and G respectively is equivalent to 4λ, and therefore the difference of phase of the planes containing A and S is $\lambda/2$; and this is also the difference of phase between any iron plane and any sulphur. If therefore AS were $AG/8$ the disappearance of the fourth order reflection would be explained.

Similarly, the sixth order would disappear if AS were one-twelfth of AG. Of course AS cannot be both one-eighth and one-twelfth of AG, but if it is one-tenth the fourth and sixth orders will both be small; indeed, calculation shows that their ionisation effects will both be negligible compared to that of the first order.

There is still one point to clear up : we cannot from the (100) observations alone determine whether the sulphur atom is to assume the position (*a*) or (*b*). Both positions lead to the same disposition in the (100) planes shown in Fig. 42. From a consideration of the (111) spectra we can show that (*b*) is correct. Perhaps this might be anticipated on the ground that the iron and the sulphur atoms could not lie so close together as in (*a*), where the distance separating them would only be one Angstrom Unit approximately ; in (*b*) the sulphur is nearly one unit from the empty corner and therefore two from the next sulphur, and this is reasonable.

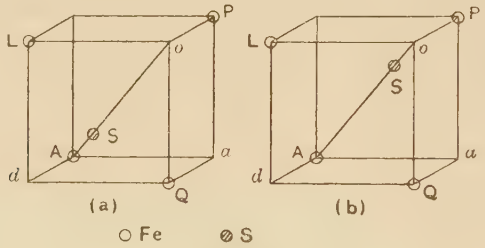


Fig. 43.

It is curious now to examine the structure in order to find a reason for the relative arrangement of the natural striations to which reference has already been made. If we project

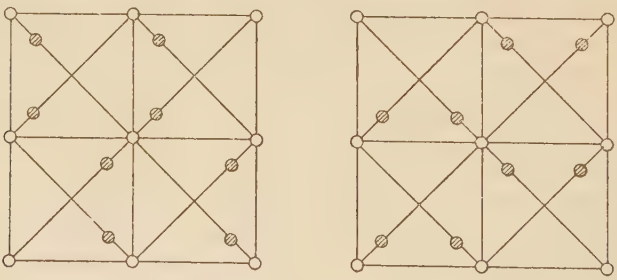


Fig. 44.

the atoms on a plane parallel to one of the cube faces we obtain Fig. 44 (left). If we turn the crystal round through

90° about any cube edge, the projection on the same plane changes to Fig. 44 (right). A certain disposition in which the projection of sulphurs was vertical has now become horizontal. The striations are really attempts at growth of certain planes, and if the disposition of the sulphurs is turned round through a right angle the same rotation will be found in the striations.

It may be instructive to point out that if the iron atoms were alone we should have a face centred cubic lattice, in which both cube corners and face centres would be lattice points. If, therefore, we took a rotation photograph about a face diagonal, such as *Bt* in Fig. 40, we should as in cases already referred to, viz. NaCl and diamond, find that the distance of the first layer line from the equator gave us the distance *BP*. But when the sulphurs of the pyrites are put into their places, *P* is no longer a lattice point if *B* is one, because the arrangements at *B* and *P* are not the same. The orientation of the two sulphur atoms grouped about *B* as a centre is not the same as that of the set at *P*. A rotation photograph will now give us *Bt*, which is twice *BP*. In fact some spots, weak no doubt, will appear half-way between the equator and the old first layer, making this latter the second layer.

Another point to be observed is that if the sulphur atoms were moved along their respective diagonals until they occupied each the centre of one of the small cubes, the calcium fluoride structure would be obtained with all its high symmetry. The lost planes of symmetry (110) would be replaced : and in the X-ray spectra the relative intensities of the different orders would change until they become very similar to those of the fluoride which we have already considered.

Iceland spar or calcite ($CaCO_3$) resembles iron pyrites in that its structure can, with the exception of one parameter, be determined by considerations of symmetry alone, as soon as the dimensions of the unit cell have been measured by the aid of the X-rays. The outstanding quantity in this case is the value of a co-ordinate which defines the position of the

oxygen atoms. Calcium and carbon atoms are spaced at equal intervals along the axis of the crystal, and each carbon is surrounded by three oxygen atoms. These lie at the corners of an equilateral triangle the centre of which is occupied by the carbon : the plane of the triangle is perpendicular to the axis. This arrangement is part of the requirements for trigonal symmetry. It is the distance between carbon and oxygen which can be varied without altering the symmetry, and cannot therefore be determined by symmetry

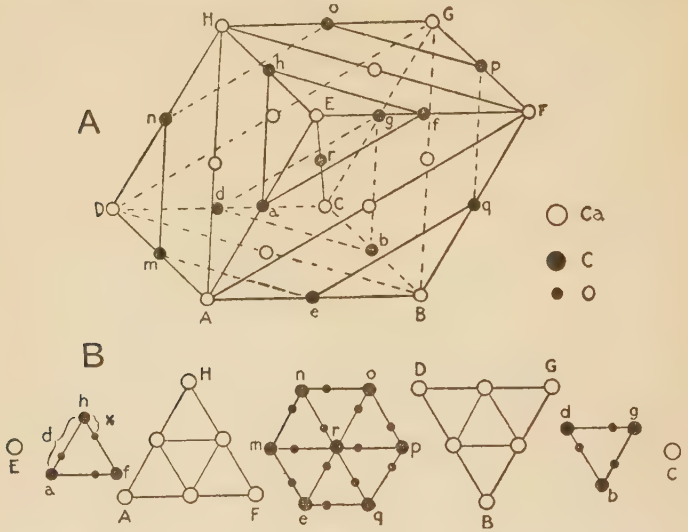


FIG. 45.—Diagram of the structure of calcite $CaCO_3$; in the second line are shown the arrangements in consecutive planes perpendicular to the axis.

considerations. We must fall back on intensity measurements, or find some other method of completing our knowledge of the design. The details are shown in Fig. 45.

In the more difficult case of quartz no less than four parameters remain to be determined after the preliminary stage has been completed. The X-ray measurements show at once that the unit cell has the form of the parallelepiped *ABCDEFGH* in Fig. 46. The angle *EAB* is a right angle and *DAB* 60°. The figure is extended to include other cells and parts of cells, so as to show the hexagonal form of the

structure. The length of AD is 4·88 A.U. and of DH, 5·37. The cell contains the substance of three molecules. This is, of course, equivalent to saying that three molecules are associated with each point on the lattice, such as A, D, H, E etc. Or, in equivalent terms which are a little more convenient for our purpose, three molecules are associated with each of the vertical straight lines AE, DH, etc., and all other such cell edges having the same length and direction, when

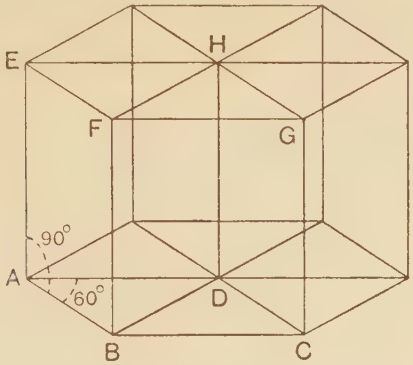


FIG. 46.—The unit cell of quartz.

the figure is extended indefinitely in every direction. The hexagonal form of the lattice is to be expected from what is already known of the symmetry of quartz. The reflection from the set of planes perpendicular to the axis, *i.e.* the set parallel to $ABCD$, is peculiar in that the first and second orders are absent ; the third is present. The interpretation is that the substance within the cell is arranged in three similar equidistant layers, the distance from layer to layer being one-third of the height of the cell. As there are only three molecules in each cell one of the three must lie in each layer. Furthermore, the crystal possesses trigonal symmetry about its axis. In order that the three molecules may as a unit possess this symmetry they must be arranged in a spiral about an axis as in Fig. 47*a*, where a, a', a'', . . . represent each of them an $Si.O_2$ group, and the axis must be of the kind called a 'screw axis.' Trigonal symmetry is secured by a combination of a 120° rotation and a shift AA' along the

axis. This brings a to a', a' to a'', a'' to a''', which is equivalent to a, and so on. Lastly, the crystal possesses yet one more form of symmetry : it has three digonal axes parallel to the lines BA, BC, and BD which are the three possible directions of cell edges in the basal plane. In order that the arrangement of Fig. 47a may have this symmetry the molecules must be so arranged that each of the lines Aa, $A'a'$, $A''a''$ is parallel to one of the cell edges ; and that in the digonal rotation about $A'a'$, for example, the molecule at a' must rotate into self coincidence, while the molecules at a and a'' interchange places, and so on. Hence, each molecule must be so arranged in the structure itself as to possess digonal symmetry. It is easy to see that this can be done with the molecule in question ; it can be arranged as in

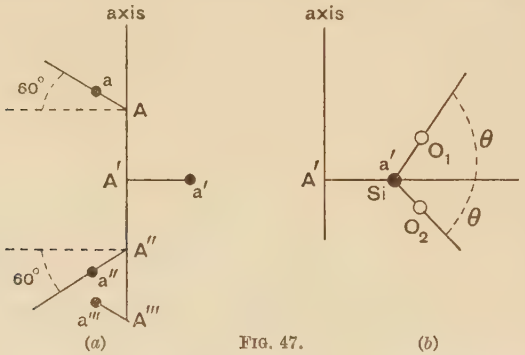


FIG. 47.

Fig. 47b, where the two oxygens O_1 and O_2 are in the same plane as $A'a'$ and the straight lines joining the silicon to the oxygens are equally inclined to $A'a'$. With this arrangement not only does the molecule at a' become self coincident after rotation through 180° about $A'a'$, and the molecule at a (*i.e.* Si +2O) change places exactly with the molecule at a'', but everywhere through the whole crystal a molecule after rotation takes the place of some other molecule.

This is as far as we can go making use only of symmetry considerations and our determination of the number of molecules in the unit cell. And we are left in ignorance of four quantities, viz. the length Aa, $A'a'$, etc., the angle

between the plane of the molecule and the axis of the crystal, the angle between $A'a'$ and the line joining the silicon to either of its oxygen neighbours, and the distance from silicon to oxygen. We have, of course, a very large number of equations which should give the values of the four unknowns, since the intensity of the reflection by every plane is a fact that must be accounted for. Unfortunately, we are

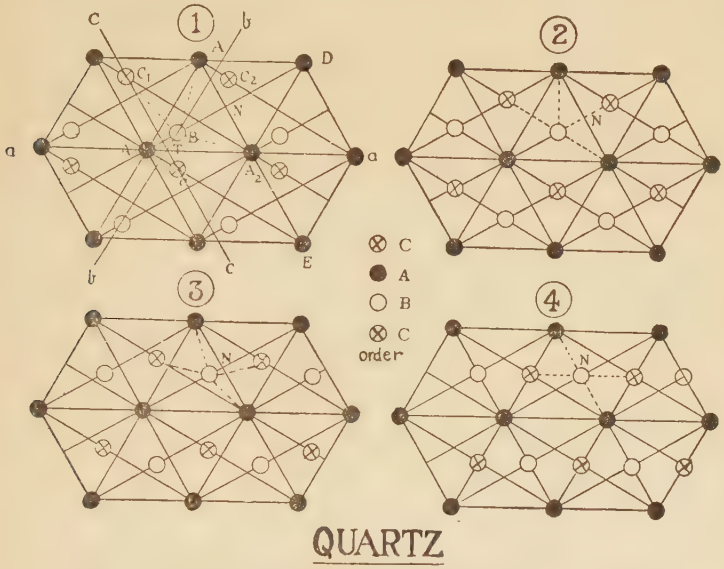


FIG. 48.—Four possible positions of the projections of the silicon atoms upon the basal plane of α quartz. Intermediate positions are also possible. The fourth is the actual projection in the case of β quartz. The silicons *A*, *B*, *C* are in consecutive equally spaced planes perpendicular to the axis, as indicated by the 'order' in the centre of the diagram. They lie therefore on a spiral.

not yet able to formulate the equations in exact terms, because we know so little of the factors on which the intensities depend. A certain amount of knowledge is in our possession, so that the equations are by no means useless, but we are hampered in our employment of a method which should be, and in the end will certainly be, sufficient for every detail. We find that we must make use of various sidelights in order to show us our way. In the case of quartz we have found for example that we can find a satisfactory solution

if we first consider the high temperature form. We argue that the low temperature form or α quartz passes gradually into the other or β quartz as the temperature is raised and passes through 573° C. ; that there is no violent change at the last, and therefore that the two forms must possess in common many elements of structure. Now β quartz is of higher symmetry than α quartz. It has all the elements of symmetry that α quartz possesses, and in addition it has three digonal axes which are perpendicular to the prism faces of the crystal. The ground plan of α quartz is shown Fig. 48, in

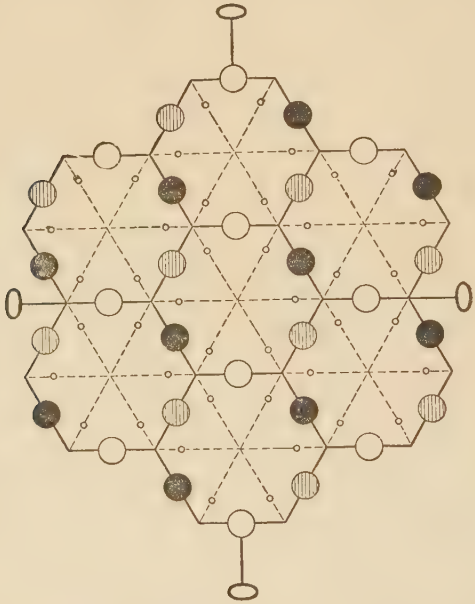


FIG. 49.—Plan of the projection of silicon and oxygen atoms upon the basal plane of β quartz. As in the previous diagram the consecutive silicons of the spiral are indicated by differences in the shading. The small circles are projections of oxygen. The hexagons in this figure are the same as those in Fig. 48 (4). In this simpler form of quartz there are three additional digonal axes at right angles to the three which are also found in α quartz. One of each kind is shown in the figure.

which the distances between the projections A, B, C of the silicons is unknown. The line aa is here a digonal axis, the other two are bb and cc. But the plan for β quartz is simpler, as shown in Fig. 49, the position of the silicon atoms in the

projection is definite, and so also is that of the oxygens with the exception of one co-ordinate, viz. the distance of any oxygen from the line joining two neighbouring silicons. As for the positions of the oxygens in the axial direction it can be shown from considerations of symmetry that they must lie half way between silicon planes. The one parameter which is now left must be determined by considerations of the intensities, and in this way the structure of β quartz has been completely found. A representation of it is given in Fig. 50.

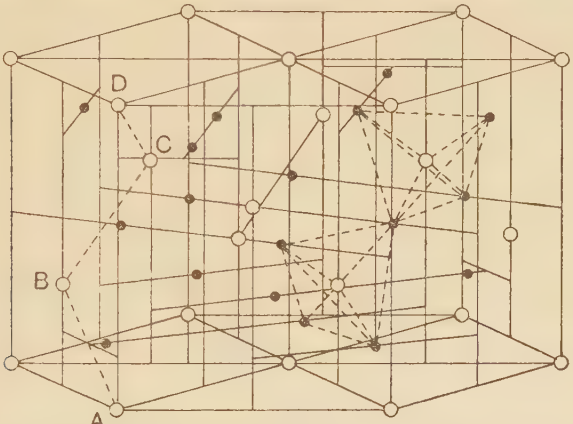


FIG. 50.—Drawing of a model of the structure of β quartz. Two sets of dotted lines indicate one of them the tetrahedral arrangement of oxygen atoms round each silicon, the other a spiral of silicons.

A very remarkable feature of the structure is the fact that the oxygens are grouped at the corners of regular tetrahedra, each oxygen belonging to two tetrahedra. Each tetrahedron contains at its centre a silicon atom. It is not easy to grasp the arrangement from a plane drawing: a model is far preferable. The oxygens and silicon of two separate tetrahedra in Fig. 50 have been specially marked in order to make the point clearer. It is not surprising that silicon, which is tetravalent, should have four oxygens grouped about it in the most regular way. It is curious, however, that each oxygen should have as its neighbours two silicons with respect to which it is not situated symmetrically. The lines joining the oxygen to the two silicons make with each other an angle of 155°.

The spiral structure of α quartz is no doubt responsible for its optical activity. The persistence of the optical activity in the β form, and the continuous change in its amount as one form passes into the other shows that the spiral form persists in β quartz with little change. There is one well-known property of α quartz which does not persist in the high temperature form, viz. that of piezo-electricity. When a piece of α quartz is compressed along any of the lines forming edges of the unit cell it develops an electric field along that line. Positive electricity appears at one end,

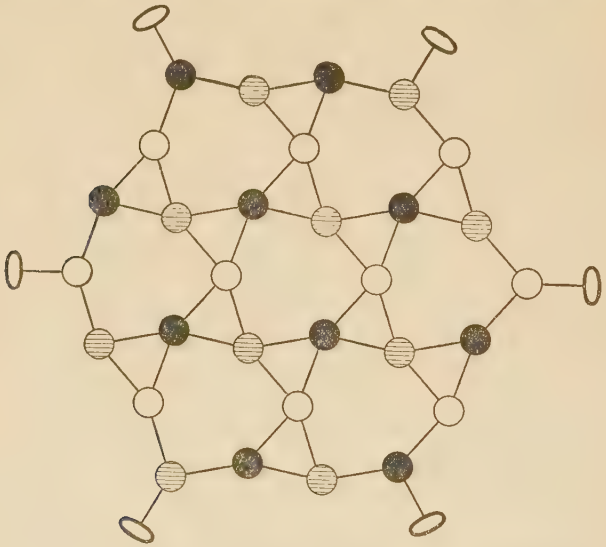


FIG. 51.—Projection of the silicon atoms of α quartz, arranged for comparison with Fig. 50.

negative at the other. The two ends of a line such as the horizontal axis in Fig. 51 behave differently, and an inspection of the figure shows at once a difference in arrangement which makes the effect possible. In β quartz, however, the small triangles of Fig. 51 have become symmetrical (Fig. 49), the two ends of the axis are now alike and the piezo-electric property has disappeared.

Thus we may look on α quartz as becoming more and more symmetrical as its temperature rises until at the critical

temperature the full symmetry of β quartz is attained. We may picture the small triangles of Fig. 51 as turning gradually on their centres, until the crooked lines become straight, and the plan assumes the form of Fig. 50. If we suppose that the whole structure is above the critical temperature, and that every trace of the original dissymmetry has disappeared, so that all the triangles are symmetrical, and that then the temperature is gradually lowered, it must be a matter of chance which way the triangles turn, in other words, which will be the sense of the piezo-electric effect. It is probable that some remainder of a previous α crystallisation or perhaps some small intrusion determines what happens. Very probably there will be several such centres which will set the fashion in different parts of the crystal, and some may cause the triangles to turn one way, some another. Thus a certain kind of twinning of common occurrence is readily accounted for. This kind of twinning does not affect the optical activity, because the screw which existed in the β quartz is not changed in sense by the transition to α quartz.

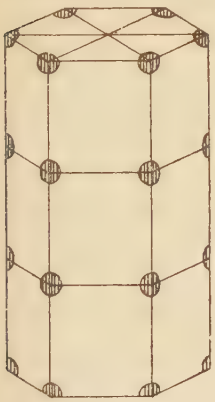
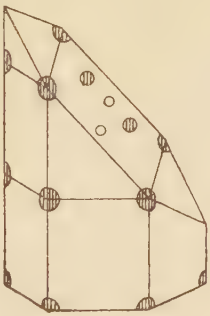


Fig. 52.



(*a*)

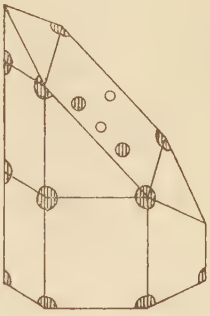


Fig. 53. (*b*)

Si O

There is a well-known twinning of the right-handed and left-handed structures, which β quartz shows as well as α quartz. The model shown in Fig. 52 is cut by a slanting plane, and

the two parts are both as shown in Fig. 53*a*. The structure is, let us say, of the right-handed variety. A similar figure, but of the left-handed variety, is shown in Fig. 53*b*. Clearly this cannot be fitted to Fig. 53*a* if the axes of the two are to be in the same straight line : as in the case when two parts like Fig. 53*a* are fitted together. But a fit can be

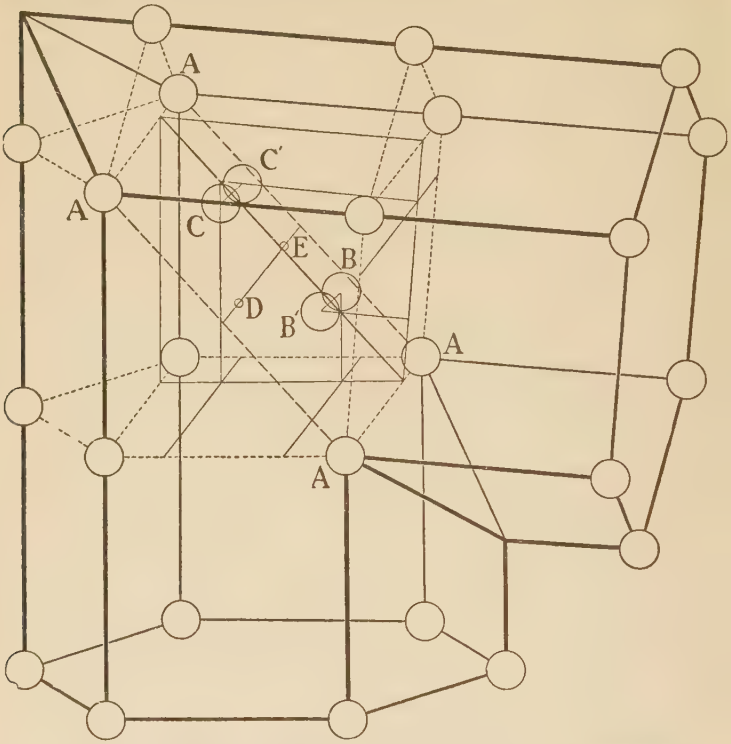


FIG. 54.—Diagram to explain a certain twinning of quartz (see text and previous figures). When the silicons marked *A* can be regarded as belonging to both prisms, the silicons *B* and *C* of one do not exactly coincide with *B′* and *C′* of the other.

effected as in Fig. 54. Twin crystals of this kind are well known though of infrequent occurrence. One such specimen is shown in Fig. 55, Plate III. The fit is not absolutely perfect : as may be gathered from the figures, a certain straining of the structure is required at the junction. But this is to

be expected. If one form were as likely as the other to proceed from or be grafted on the original portion there would be no reason why the crystal should grow regularly at all.

In this case one of the two blocks is the mirror image of the other : the screws are therefore of opposite senses. This was not true of the first case of twinning which we considered.

These examples of twinning may be looked on as illustrating the explanation of known properties, such as may always be expected to follow from a better knowledge of structure.

As soon as the structure of β quartz has been determined the way is made ready for an attempt on the more complicated low temperature structure. It is assumed that the one form changes into the other by a process which proceeds steadily, though it may be accelerated at the last. It is not to be expected that the total change is very great as there is so little change in the general character of the crystal. In plan the nature of the change is shown by the rotation of the small triangles of Fig. 51 as already explained. In elevation there are also changes, in fact there are now four parameters and therefore a somewhat complicated movement has to be determined and calculated.

A solution has been reached through the consideration of the changes in the intensities of the reflections by various important planes as the temperature is changed and the transition from one form to the other takes place. It appears that the triangles of Fig. 51 have turned through about 9° from their symmetrical β positions, and that the regularity of the oxygen tetrahedra is not fully maintained. But the full description would be too lengthy for our present purpose, which is in the first place to differentiate the methods adopted in dealing with the determination of various structural features. At the same time we wish to show how the details of the structure as they are found can be correlated to physical properties, since this correlation and all that may flow from it must naturally form a principal object of the whole work.

We have tried to show that up to a certain point symmetry considerations and a certain use of the X-ray measurements may bring us to an exact knowledge of the structure of a crystal.

In most crystals, however, a number of parameters remain to be found before the structure is fully known : before that is to say each atom has been placed in position. Pyrites, calcite and β quartz have one such parameter ; α quartz has four. The number of parameters increases with the complexity of the compound, and the diminution in crystal symmetry. We have seen that measurements of the intensities of reflection help us on our further way ; in the cases quoted they have in fact been sufficient to give a satisfactory final solution.

But as the complexity increases so do the difficulties. Eventually it must be possible to read every detail of structure in the measurements of the X-ray spectrometer and the X-ray photograph ; but in the vast majority of cases our efforts are only partially successful. On this account we look for other aids, and we find, indeed, that there are various ways to which we may approach nearer to the final solution. We shall say something of these auxiliary methods in a little while. We shall also find it helpful to consider more systematically the various stages of the analysis, and this we do at once.

CHAPTER IV

SPACE GROUPS OR CRYSTAL ARRANGEMENTS

We have already observed that there are three stages in the analysis of a crystal. The first is complete when we know the dimensions of the space lattice, or, which is the same thing, of the unit cell. The unit cell usually possesses various symmetries.

Next, the contents of the unit cell can be divided into similar atomic groups which we may call cell-elements, or simply elements when there is no danger of confusion with other uses of the word. The cell-element has no symmetry ; but combination of cell-elements gives symmetry to the cell. Each element is like every other except, as we shall see later, for right and left handedness, and has similar surroundings, but the different elements in the cell are differently oriented. All unit cells are, of course, oriented alike.

When the arrangement of the elements within the cell has been found the second stage of the analysis is finished. This stage is usually spoken of as that of the determination of the ' space-group ' : the connection between the two terminologies will appear presently.

In the third and far the most difficult stage we are concerned with the relative positions of the atoms within the cell-element. When finding the complete structure of such comparatively simple crystals as rocksalt or diamond we may merge the last two stages into one : it is not of great importance to mark the point at which the dividing line is reached and passed. But when we come to the more difficult cases we find it convenient to consider the second stage more carefully. We can always complete it unless our technique fails ; and it is well to note when we have done so. It may be we can for the time go no further, and must be content

to describe the position reached ; but we may more hopefully consider that we have established a base for a fresh advance.

We proceed to consider the rules that govern the arrangement of the cell-elements, or, in general, of bodies that are all alike. We find at once that there is a limit set to the number of arrangements that are possible. It is indeed in this fact that we find the usefulness of giving separate consideration to the theory of cell-elements.

We might be inclined to say at first that there is no limit to the number of ways of arranging atoms or groups of atoms or cell-elements or things in general. This is perfectly true if there are no conditions to be obeyed. But when the condition is made that all the groups or elements or things are exactly alike, and each is to be arranged in exactly the same way with respect to its surroundings, then there *is* a limit to the number of arrangements that are possible. The number is two hundred and thirty. It seems odd, at first sight, that so definite and arithmetical an answer can be given to such a question ; but it is simply the result of a straightforward count. The full reckoning is too long to be included within the limits of a lecture, but it is so important and, I think, interesting that it is well to give it some partial consideration. Moreover, on our way through such a count we discover the rules regarding symmetry and the distinctions regarding form which are the essence of crystallography.

The subject of crystallography is usually based on a consideration of the outward appearances which crystals present, and therefore we depart somewhat from custom when we attack at once the general question of the number of possible arrangements of similar things. There is, however, a distinct advantage in doing so, because the X-ray methods allow us to go more to the root of the matter than the optical methods, and the analysis is better developed from the more fundamental treatment.

Let us imagine ourselves therefore to be provided with a number of bodies all alike, these bodies representing the atom or groups of atoms which are found in Nature ; and let us proceed to pack them together and to count the number

of ways in which the packing can be done. And suppose that in the first place we consider the problem in two dimensions only. The principles are the same in two dimensions as in three, and the methods are much simpler to describe and to grasp because we are all more experienced in the consideration of the simpler conditions; moreover, plane drawings are so much easier to make than three dimensional models.

We take a plane surface, such as a table, and we have at hand a number of flat objects, cut out of cardboard and having no symmetry of form. A triangle will do, or a shape like a large comma, such as is used in some of the following illustrations. No two sides of the triangle are to be equal, but otherwise there is no restriction on its form. The fundamental condition is always to be borne in mind, viz. that in the structure each element is to have the same surroundings. The only qualification to this statement will be that, as we shall see later, there may be both right-handed groups and left-handed groups, but even then a right-handed group is to have right-handed surroundings, and *vice versâ*.

In the first place, we may put our bodies together as in

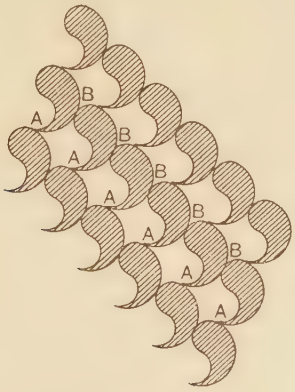


FIG. 56.

Fig. 56. Here there is no symmetry in the arrangement. If each one represented a group of atoms the implication would be that this was a way in which the groups with their

complex fields of force dovetailed into each other : the tip of one comma is in contact with a particular point on the back of another ; the contacts marked *A* are all alike. So are the contacts marked *B*. For some reason the objects or groups take up these positions in preference to others, and the satisfaction of this preference throughout the structure gives it its regularity and its special form. If we take some point in each specimen to represent that specimen, say the tip of the comma, we find that such points are the points of

Fig. 57.

a plane lattice (Fig. 57). One comma goes to each point, or to each cell of the lattice, no matter whether or no the comma is fully contained in the cell. If the points at which the commas preferred to be in contact were other than what they are the lattice would take a different form. We consider that this arrangement is to be reckoned as *one* of our possible arrangements for it has definite characteristics, namely, a cell of rhomboidal form, and an absence of all symmetry. For a different group of atoms which might be considered to be represented by a different comma, the lattice would differ also in the sides and angles of its cell, but the one arrangement covers all such variations.

A different arrangement is shown in Fig. 58. In this case the same elements are used, but half are differently oriented from the other half. Taking any one of one set in company with any one of the other sets there is a point between them, such as *P*, about which a rotation of 180° will bring each

exactly into the position first occupied by the other ; indeed the whole figure becomes clearly self-coincident after such a rotation. This deserves to be called a new arrangement, because if the association of one body with another is determined by mutual forces then there must be a distinct difference between the forces in this case and in that which we considered first. Moreover, bodies constituted on the two plans must show external differences. In the first case the commas all point one way, and the properties of the body must share this singularity : it will have ' polar ' properties. In the second case this singularity disappears : the body

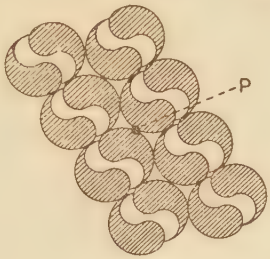


Fig. 58.

has acquired a certain symmetry. This effect is naturally to be found also in the three dimensional problem, that is to say in the crystal. Some crystals are polar and some are not. We do not attempt at this stage to explain why nature should strive after symmetry in this way : we are content for the time to say that the reason is to be found in some characteristic disposition of the atoms within the element.

And now we come to a very interesting point. Let us allow ourselves to have at our disposal, in addition to the original groups, other groups which are the images of the first kind across any line in the plane in which we are forming our arrangement. It is the commonest thing in Nature to find parts of living objects which are right and left to each other, hands, feet, eyes, the petals of flowers, the ribs of leaves, and so on. When we go down to the first elements of construction we must find the same property, since the big grows out of the small. We ought, therefore, to take into consideration

both right- and left-handed or ' enantiomorphous ' elements, to use the language of crystallography. If we do this we find other possible arrangements.

Consider Fig. 59*a* for example. There are equal numbers of right-handed and left-handed elements, and they are so

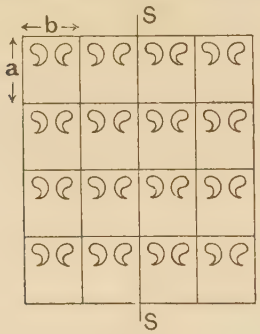


FIG. 59*a*.

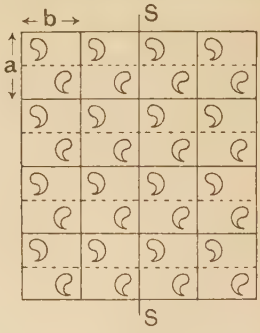


FIG. 59*b*.

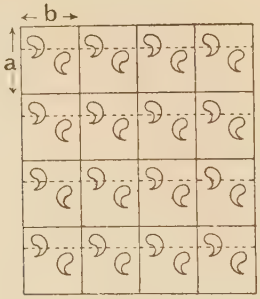


FIG. 59*c*.

placed that the surroundings of every element are of one or other of two kinds, which like the forms of the elements are the reflection of each other in a mirror. This is as it should be since we have always to satisfy the fundamental condition which was set for us at the outset. Such a disposition will, of course, have its effect on the body as a whole, which will therefore be symmetrical about a certain line in the plane. This is a third arrangement.

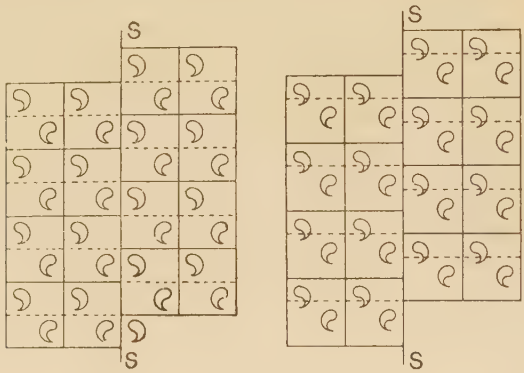
In Fig. 59*b* the same elements are arranged a little differently. In Fig. 59*a* any element of one kind is the reflection of an element of the other kind across a vertical line properly

placed. In Fig. 59*b* each element becomes coincident with an element of the other kind when first reflected over such a vertical line and then made to slide parallel to the line for half the distance that would be required to recover the first arrangement, *i.e.* to bring left- and right-handed elements opposite to one another again. This is clearly a new geometrical disposition : and if the elements forming some body adopt it they must possess some special characteristic. It fulfils the fundamental condition that every element must possess the same surroundings except, of course, in respect to the alternative of right and left. Also the body as a whole, viewed of course from points in the plane, will show symmetry across the vertical line as in Fig. 59*a*, although the arrangement of Fig. 59*b* does not show that symmetry. The reason for this is that an eye placed in the plane does not see the plan shown in the figure, but only edges, and these will look exactly alike.

Here then we find that two different arrangements will present the same appearance from the outside : the analogous case in three dimensions is of great importance as we shall presently see.

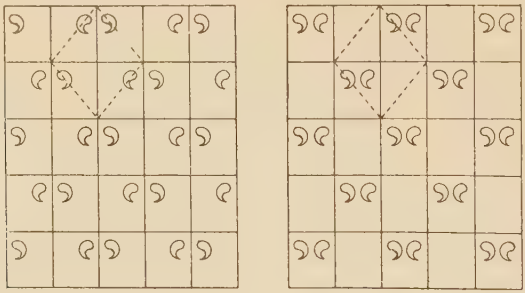
But, we may now ask, if this particular combination of reflecting and shifting brings a new arrangement into view, can we not find variants of it which will yield further arrangements ? The answer to this question is that the amount of shift cannot be altered without disobedience to the fundamental condition. If, for example, the shift has any other value than that of Fig. 59*b*, such as is shown in Fig. 59*c*, the surroundings of a comma with a tail pointing one way are not the same as those of a comma the tail of which points the other way, even when allowance is made for the fact that one is right-handed and the other left. The same point is possibly clearer if it is looked at in a somewhat different way. If the right-hand half of Fig. 59*b*, which represents the arrangement already approved, is shifted as a whole upwards until there is a match immediately across the dividing line *SS*, Fig. 60*a*, the whole of the figure on one side of the line is the reflection of the whole of the figure on the other : there is

symmetry across the line. But if the same treatment is given to the arrangement of Fig. 59*c* where the shift has not the proper value the want of symmetry across *SS* becomes obvious (Fig. 60*b*).



(*a*) FIG. 60. (*b*)

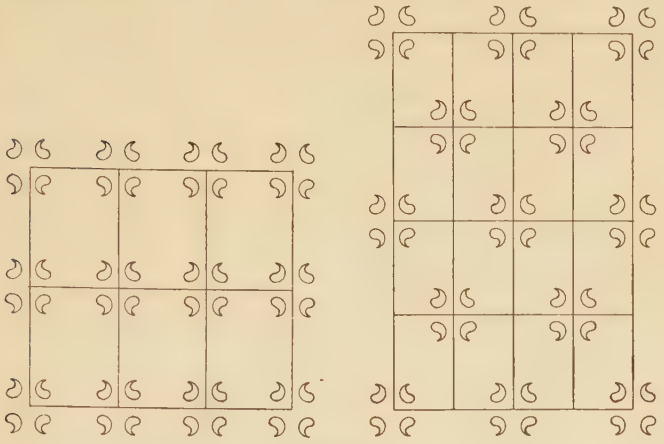
We have, in fact, come to the end of the arrangements on this basis, but we can find one more by taking another form of the lattice cell. For we can also obtain symmetry across



(*a*) FIG. 61. (*b*)

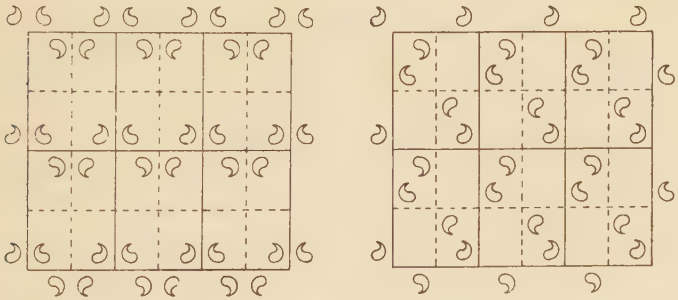
a line by the arrangement of Fig. 61*a* in which the lattice cell is obviously a rhombus. In this case the attempt to find another arrangement by introducing a shift leads to nothing new, as is shown in Fig. 61*b*, because this arrangement is really the same as that of Fig. 61*a*. In each case the cell is a rhombus, at every corner of which is a group itself symmetrical about the vertical line.

We again introduce new arrangements when we so dispose of the elements that there is symmetry across both vertical and horizontal lines ; in this case we require four units for



(*a*) FIG. 62. (*b*)

the completion of each cell in the lattice. In Figs. 62*a* and 62*b* are two arrangements which obviously possess such symmetries, and in Figs. 63*a* and 63*b* are two more which possess



(*a*) FIG. 63. (*b*)

the same symmetries though not so obviously. They are derived from Fig. 62*a* by a single shift in the first case and a double shift in the second. There are no more than four : if we try to find new arrangements by imposing the shift process on Fig. 62*b* we do not succeed, we only arrive at forms which are equivalent to what we started with.

Again then we find that more than one arrangement will give the whole body the same two symmetries, viz. symmetry across each of two lines at right angles to one another.

We may go further and find arrangements in which the elements are in groups of three, so disposed that if the whole is turned round 120° in its plane of the table each element occupies exactly the same place on the table that was previously occupied by another element. This is illustrated in Fig. 64. The whole body possesses a trigonal axis which is perpendicular to the plane. By adding an equal number of the other sort, that which is enantiomorphous to the first sort, we can obtain symmetry across three directions in the plane, as is shown by Fig. 65. Or we may arrange the

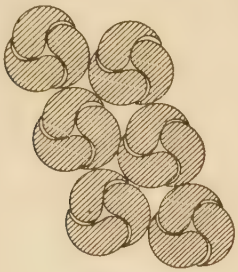


Fig. 64.

Fig. 65.

elements so that there is a tetragonal axis or a hexagonal axis, *but not any other kind of axis*. There cannot, for instance, be one in which the four right angles are divided into five parts by the successive acts of rotation ; nor can there be seven, nor eight, nor any higher number. That is because the plane can be divided regularly into triangles, squares and hexagons, but not into pentagons or octagons. But there is no necessity to go further. For it will now be clear that there can be a limit to the number of possible arrangements of the elements under the specified conditions. Also, it will be clear that if these arrangements were to be classified by their appearance to an eye in the plane, which could see the edge but not the inside of the pattern, then many of the arrangements could not be distinguished one from the other.

To pass from two to three dimensions is to meet with much greater complexity, and a much larger number of possible arrangements. But the procedure of enumeration runs on exactly the same lines. As in the simpler case several different arrangements may result in the same external appearance of the crystal. Let us take one or two examples.

We have now to arrange *in space* numbers of objects, each one of irregular, unsymmetrical form, but all exactly alike, in such a way that each has exactly the same surroundings. There is, as before, one qualification of the term 'exactly alike,' namely, that right- and left-handed groups and arrangements are permitted.

Let us consider two only of the many types of symmetry. Let us first take the case where the completed structure shows

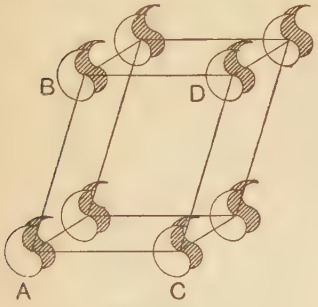


FIG. 65*a*.

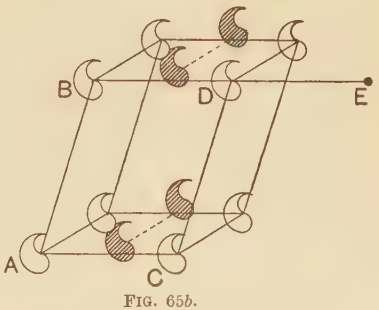


FIG. 65*b*.

a plane of symmetry and no other symmetry ; and, secondly, the case where a second plane of symmetry is added to the first. We take equal numbers of right- and left-handed elements or groups of atoms ; we are particularly avoiding the use of the word molecule. Suppose that our elements are represented as before by bodies like commas, of which we now distinguish the two sides from one another : one side may be black, the other white, as in Fig. 65*a*. The arrangement in the figure clearly possesses the specified symmetry. The commas are not drawn to touch each other this time ; for after all they are merely representative of groups of atoms of which it can be understood that they interlock with each other. The straight lines show the unit cell of the lattice ;

the shape of the cell being determined by the form of the groups, or, which comes to the same thing, the nature of the interlocking. Four of the faces of the cell are rectangles, the other two are parallel to the plane of symmetry : which must be the case if there is the symmetry specified.

Another arrangement is shown in Fig. 65*b* where the right-handed element is derived from the left by reflecting across some plane, which is parallel to the face that has no right angles, and subsequently sliding the reflected element in a direction parallel to one of the lines joining two elements in the same plane, the amount of the shift being half the distance between the two elements chosen. In the figure the shift has been parallel to AC and equal to $AC/2$. This second arrangement will, like the first, give the completed crystal an appearance of perfect symmetry across a single plane. There is no variety of this last arrangement to be obtained by choosing any other pair of elements in place of A and C : *e.g.* A and B, or A and D, or A and E, where E is some more distant element in the same plane as A ; for all such have the same description. We chose A and C in our first example, which elements are at the corners of the lattice cell as drawn in the figure, but we might have drawn the cell so that, for example, AE was one edge, and we should still have been able to describe our second arrangement as one in which there was a shift parallel to an edge and equal to half of it. If the cell has the form in the figure these are the only two arrangements to be found that satisfy the fundamental condition. In this case then there is a crystal form presenting definite and characteristic symmetry to the eye, while the form may be due to either of two arrangements between which the eye cannot distinguish. The X-rays alone can detect the difference : they decide in the following way.

Suppose that we view the lattice along a direction perpendicular to the plane of symmetry, and let $ABCD$ be the face of a single cell (Fig. 66*a*). If the arrangement be the first of the two just considered the reflected elements belonging to the cell are behind those that are drawn, and are hidden

by them. The set of planes which are perpendicular to the paper and pass through AB and CD respectively have for their spacing the perpendicular distance between AB and CD, which spacing can be found by the appropriate use of the X-rays.

In the second arrangement the reflected elements move out from behind $ABCD$, and are shown in Fig. 66*b* ; the amount of scattering material which was concentrated along such lines as AB and CD is now halved : the half which is removed is lying along lines such as EF. We have now a set of parallel planes, all equally loaded, the spacing of which is only half what it was before. The X-rays at once demonstrate this point ; so that if we know that the unit cell is

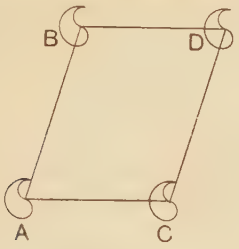


FIG. 66*a*.

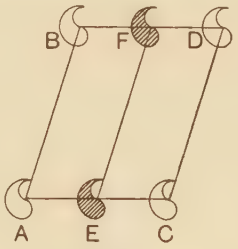


FIG. 66*b*.

really of the form $ABCD$ the X-rays settle which of the two arrangements has been adopted. Of course any other shift than that which is parallel to AC would be detected in similar fashion.

But, it will naturally be said, we determine the size of the cell by measuring spacings : if we had chosen these planes as one of the sets to measure should we not have been misled, and have noted the size of the spacing at half its true value ? Should we not have found a volume for the cell which was only half its true volume, assuming its other dimensions to have been determined correctly ?

The answer to this question is that we should indeed have made the mistake in question if we had made no other determinations than the bare three which are required to find spacings in three different directions. We must always make more than three. We must remember that if $ABCD$,

$A'B'C'D'$, is the real unit cell, the spacings of an infinite number of sets of planes can be calculated from the cell dimensions, and it will be no more than an exception if some sets of planes give measured spacings which are not in agreement with calculation. Let us take an example : let us suppose we look along the edge AB, so that the cell in the second case has the appearance of Fig. 67, and let us suppose that our commas seen from this new direction are as represented. We must not suppose them to look alike from this

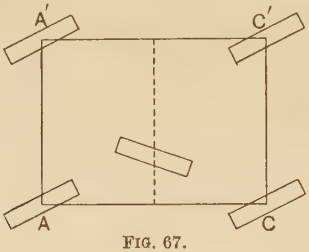


FIG. 67.

point of view ; there is no reason why they should. The comma was to represent, it will be remembered, a group of atoms having no symmetry at all.

The spacing of the set of planes parallel to the reflecting plane is equal to AA', for $AA'C'C$ is a face of the unit cell. The introduction of the reflected elements as shown does not affect the determination of the spacing by the X-rays ; it does not, as in the former case of Fig. 66*b*, introduce new layers exactly interleaving the old layers and exactly similar to them.

The same may be said of any other set of planes except certain sets which, like that first mentioned, are perpendicular to the plane of the diagram (Fig. 66). There can, therefore, be no mistake about the true dimensions of the lattice ; the exceptions to the general rule are obvious exceptions, and valuable because they tell us which of two possible arrangements is actually adopted in the crystal.

The X-ray examination has therefore already carried us on two stages beyond the point which the observation of external form can reach. It has told us the absolute dimen-

sions of the lattice, whereas the goniometer could only tell us the mutual ratios of the lengths of the sides of a cell which was not necessarily a unit cell; and it has enabled us to differentiate between two arrangements which were indistinguishable otherwise. The goniometer assigns the crystal to its proper *class*: the thirty-two classes differing from one another in their degrees of symmetry as revealed by their external form and other physical characteristics. The additional information supplied by the X-rays determines in general which of the two hundred and thirty arrangements is adopted by the crystal. Each class is subdivided into many arrangements: the goniometer brings us as far as the class; the X-ray spectrometer takes us to the arrangement. The particular class which we have just been considering is known to crystallographers as the 'Monoclinic Domal Class' (Tutton's *Crystallography*, vol. i. p. 256). The two arrangements described are known as C_s^1 and C_s^2. There are two other arrangements in this class known as C_s^3 and C_s^4; but we need not follow these considerations any further.

The X-ray spectrometer can indeed take us all the way; with one important and a few minor reservations. It can measure angles as well as the goniometer; indeed better, for its measurements are independent of the state of the faces of the crystal, and it is not even necessary that any faces should be shown at all. It fails in that it cannot tell one end of a polar crystal from the other, as we have already observed in the case of zincblende (p. 69). But such a difference is obvious from the form of the zincblende crystal, and from other physical characteristics. If it is heated, for example, so that the electrically charged constituents of the atoms are disturbed in their delicate balance, electricity of one sign appears on the one side *A* and of the other sign on the side marked *B*. There is, so to speak, a zinc side and a sulphur side of the crystals; and the two exhibit different properties. The polarity of the crystal is immediately detected by its external behaviour: it is not immediately detected by X-rays. In the end, nevertheless, the X-ray analysis of zincblende discovers the polarity of the crystal,

for it determines the structure completely, and the polarity is then revealed. This is not always so ; the X-rays may sometimes be unable to determine the proper arrangement until observation of external characteristics has determined the class, and shown whether or no there is polarity.

Let us consider very briefly one more crystal class ; that which shows the symmetry across two planes at right angles to one another. More than one form of lattice is consistent with such an effect, but the simplest is that which permits the unit cell to be drawn with all its angles right angles as in

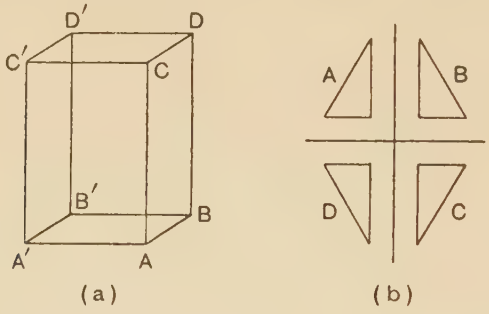


FIG. 68.

Fig. 68*a*. We suppose that the crystal is to show symmetry across planes parallel to *ABCD* and *ACC′A′* respectively ; but not across a plane parallel to *ABB′A′*. The class of crystal is known to crystallographers as rhombic-pyramidal, or rhombic-hemimorphic (Tutton, *loc. cit.* i. 227). In order to obtain so much symmetry four elements each possessing no symmetry at all must be allotted to each unit cell. They may conveniently be represented in this case by right-angled triangles, as the edges have definite directions which make it easier to grasp their position in the figure. The upper side of each triangle is supposed to differ from the lower, since there is to be no plane of symmetry parallel to *ABB′A′*. There are two varieties of triangle, *A* and *C* of one kind, *B* and *D* of another : a triangle of one kind cannot be superimposed on one of the other. As already stated we suppose these right and left variations to be permitted (Fig. 68*b*.)

The simplest arrangement of the elements in the cell is that shown in the first example in Fig. 69, where the group of four elements shown in Fig. 68*b* is placed at each corner of the cell. It will be remembered that in the whole lattice there are just

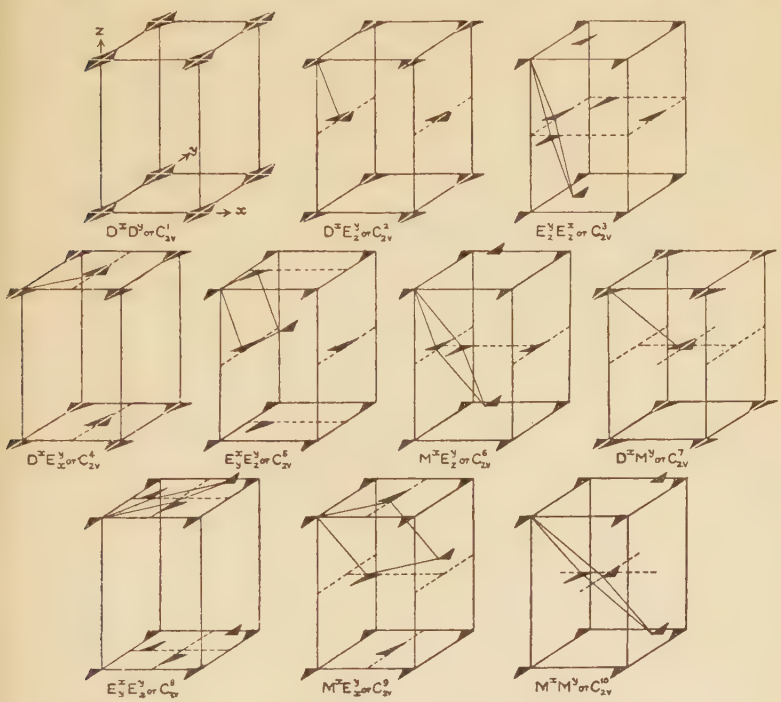


FIG. 69.—Ten arrangements of the four elements (Fig. 68 (*b*)), each of which gives structural symmetry about two planes at right angles. Below each figure are two symbols. One of them, *e.g.* C^6_{2v} is that by which it is known in space group classification, as explained in the text. The other describes the arrangement. For instance $D^x E^y_z$ means that *B* is derived from *A*, and therefore *D* from *C* by Direct reflection across the (100) face: while *C* is derived from *A* and therefore *D* from *B* by reflection across the (010) face followed by a translation parallel to the *Oz* Edge. M^x means a reflection across the 100 face followed by a translation parallel to either line joining a corner of the 100 face to the Middle of that face.

as many cells as there are corners. Only one-eighth of the group placed at a corner really belongs to the cell that is drawn, since seven other cells meet the cell in that same corner, and each claims one-eighth of what is placed there.

This first arrangement can be developed into nine more by appropriate reflections and shifts after the manner already explained when treating the two dimensional problems of Figs. 62 and 63. The whole ten are shown in Fig. 69. There are also other types of lattice besides the simple lattice of Fig. 68*a*. These are shown in Fig. 69*b*. Seven arrangements belong to the first of these, three to the next and two to the last ; but it takes much space to draw them all. The point to be made is that there are in all no less than twenty-two possible arrangements of the four unsymmetrical elements which all give the required symmetry. All belong to the one ' class,' as defined by external symmetry alone ; but all differ in their internal arrangements,

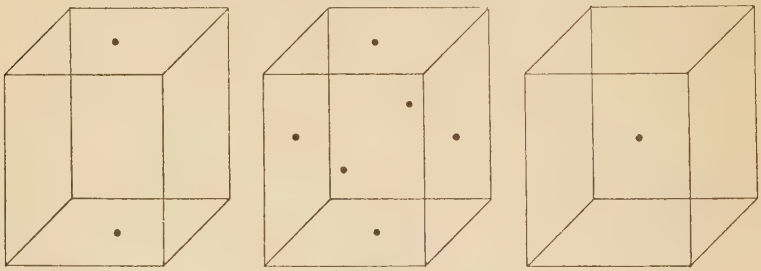


FIG. 69*b*.

and the differentiation within the class can be made by the X-rays. For instance, resorcinol on the usual external crystallographic evidence is assigned to the orthorhombic-pyramidal class : the X-ray evidence further defines it as having the arrangement known as C_{2v}^{10}.

This class is one of the most varied in respect to its possibilities of internal arrangement. In all there are thirty-two classes and 230 arrangements.

We have used the word ' arrangement ' as suitable to the mode of exposition which we have followed. The term space group is most commonly employed. Starting with a single element, each arrangement can be defined as a derivation from that element by successive reflections across certain planes and rotations about certain axes, with or without shifts of the kind mentioned above. This group of operations

in space is as much descriptive of the final result as is any of the pictures of say Fig. 69 ; and has been generally adopted in the mathematical development of the subject, and hence the term ' space-group.'

It should be observed that there is no body of accumulated information about any space group or arrangement. It is a convenience to know that such and such space-groups are possible, and to tabulate the X-ray tests for each group, since this leads to quicker working. But when the actual arrangement has been found the identification with one of the known possibilities is no more than an act of labelling, and otherwise brings no addition to knowledge.

The determination of the arrangement or space-group of a crystal marks the end of a second stage in its analysis. The first, it will be remembered, ended in knowledge of the form of the lattice ; we have now learnt also the particular way in which the elements in the lattice cell are arranged.

We have been using the word element to denote that group of atoms which is repeated continually within the crystal in such a way that its surroundings are always the same. We have allowed ourselves to consider that an element can exist in two forms, one of which is the reflection of the other across a plane ; any plane will do, because the position of the plane does not alter the form of the reflection. In the crystal class, which we have just been considering, four such elements were required in each unit cell so that the symmetry of that class might be attained.

We are now led naturally to ask the following question : What is the connection between this element and the molecule in any given case ?

It is found that the connection is always very close, but that the element and the molecule are not necessarily the same. A molecule frequently contains, or perhaps we should say is made up of several elements, and sometimes an element contains the substance of more than one molecule. Let us take the naphthalene crystal as an example of the former case. It belongs to the class designated by crystallographers ' Monoclinic prismatic.' The shape of the lattice

cell is shown in Fig. 70, in which OB is perpendicular to the faces $OAGC$ and $BFED$. There is symmetry across planes perpendicular to OB, and also there is digonal symmetry about any axis parallel to OB ; that is to say, if the crystal were turned round through 180° about such an axis the result of the rotation would be imperceptible ; the crystal would present the same appearance as before.

In order to obtain such symmetry four elements must be allotted to each cell. There are four possible modes of arrangement. It appears that the actual arrangement can be

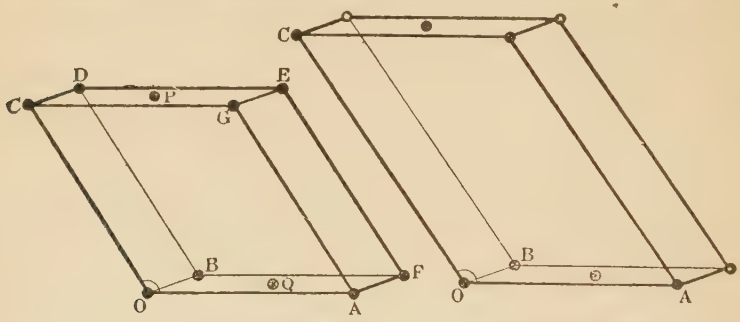


FIG. 70.

	$OA=a$	$OB=b$	$OC=c$	$AOC=B$
Naphthalene, -	8·34	6·05	8·69	122° 49′.
Anthracene, -	8·58	6·02	11·18	125° 0′.

described in the following way. Place an element which we will call A at O, and others like it at the other corners. These last can all be supposed to be derived from the element at O by shifts which are parallel to the edges and equal to their lengths ; the original orientation of the element being always maintained. This, as explained before, is equivalent to assigning one element to the cell. A second element, which we will call B, is the reflection of A in some plane perpendicular to OB (the position of this plane is so far indeterminate), but the reflected element is shifted parallel to OA through a distance equal to the half of OA. The third and fourth elements in the cell, viz. C and D, are derived from A and B respectively, by rotating them through 180° about some axis parallel to OB (the position of the axis is otherwise

indeterminate), and afterwards shifting them parallel to OB through a distance equal to the half of OB. This arrangement seems to be of frequent occurrence in organic crystals.

The relations of four such elements to one another are interesting. An element of the A type is the reflection of an element of the B type : it is the same as one of the C type turned round 180° about a certain axis ; while A and D are the inverse of one another about a certain point, or, in other words, the two taken together have a centre of symmetry. These relations can be studied in the form of a diagram :

A	reflects into	B
rotates into	centre of symmetry	rotates into
C	reflects into	D

The form and dimensions of the lattice of naphthalene, as determined by X-rays, are shown in Fig. 70. We can calculate the mass contained in the unit cell, and we find it to be 423 A.U. The units employed here are Angstrom Units ; that of length being 10^{-8} cm., of area 10^{-16} cm^2., and of volume 10^{-24} cm^3. The unit of mass is 10^{-24} gr.

Now the molecular weight of the naphthalene molecule is 128, and its actual weight is, therefore, taking the weight of the hydrogen atom to be 1·64 A.U., equal to 210 A.U.

To each unit cell, therefore, or, what is the same thing, to each point of the lattice belong two molecules of the composition $C_{10}H_8$. What then is the relation of the two molecules to the four elements belonging to each cell ?

Clearly, the molecule must contain the substance of two elements ; but the experimental data are insufficient at the stage we have reached to establish a closer connection without drawing in evidence from fresh sources.

It is practically certain that the molecule $C_{10}H_8$ is identifiable, and held together by stronger ties than those which bind any molecule to its neighbours ; for, when the substance melts, it resolves itself easily and directly into such molecules.

Each of the two molecules must, therefore, be capable of division geometrically into two parts, the relations of the four parts to each other being those of the four elements A, B, C, D. The point then arises, does one of the two molecules, as we picture them, from chemical evidence, in the diagrammatic form consist of A and B, or A and C, or A and D ? The X-rays do not tell us directly, but perhaps we may argue that a combination of A with B is unlikely, because it would mean that half the molecule is the reflection of the other shifted a distance equal to 4·17 Angstrom Units, and there is no chemical evidence for that. So also the combination of A with C seems objectless ; but if we pair A with D we make the molecule to contain two parts which taken together have a centre of symmetry, and we impose no exact geometrical relation such as that of the 4·17 shift, when A and B are associated, or 3·025 in the case of A and C. It seems quite reasonable to suppose that the molecule of naphthalene has a centre of symmetry ; there is such a centre in the diagram as ordinarily drawn. It is true that the diagram has direct reflection symmetries also, but the molecule in the crystal evidently has none, because its surroundings have none. For the molecule is known to us as a seat of forces extended towards its neighbours, and if there is no symmetry in the arrangement of the neighbours we cannot recognise any in the molecule.

If our skill in the interpretation of the X-ray diagrams were great enough to enable us to fix the position of every atom the problem would be solved directly. We cannot yet do so much as this, in the case of naphthalene, but there is still something to be told of the capacities of the method.

The molecule of naphthalene therefore contains two elements each without symmetry, of which four go to the making up of the monoclinic prismatic cell. Sometimes we find much higher numbers. The cubic cell of rocksalt has so much symmetry that forty-eight unsymmetrical elements are required in order to produce it. But there is only one

molecule of sodium chloride in the cell ; and though a separate molecule cannot be supposed to be made up of the forty-eight, yet each separate atom of sodium (or chloride) can be supposed, in consideration of the peculiar and simple structure, Fig. 32, to be so made up in respect to its relations with its neighbours.

On the other hand we sometimes find cases where there are more molecules in the cell than the number of elements, as, for example, in the cases of fumaric acid, and α-naphthylamine. In each of these crystals the element contains the substance of three molecules. The element has no symmetry of its own, so that the three molecules are not only

(*a*) FIG. 71. (*b*)

without individual symmetry but differ from one another in their manner of entering into the crystal structure. The three, we may say, make a new molecule ; but if we use these words we must take them to mean no more and no less than the previous sentence implies. An ' association ' in chemical technology means a grouping of molecules under special ties, which keep the group distinct from other molecules in the neighbourhood ; nothing is implied as to the symmetry of the group. The grouping of three molecules to form one element in the crystal cell does not imply directly that there is any bond between them of greater strength than the bonds that unite one of these molecules to any other of its neighbours in the cell.

In the Fig. 71(*a*) three objects are drawn to represent chemical association ; they are specially tied together where they meet, and the group exists as a unit in a gas or a liquid.

They may or may not be symmetrically arranged, actually there is a line of symmetry in each group. In Fig. 71 (*b*) three kinds of object are represented in crystal association. They are *not* symmetrically arranged, and they may or may not be specially tied together. The two forms of association may prove to be connected. For example, the known association of sulphur atoms in the vapour seems likely to be connected with the apparent grouping in the crystal ; but for the present there is no actual proof.

When we have determined the arrangement or space-group we have come to the end of the second stage of the X-ray analysis of the crystal. The first stage was accomplished when we found the form and dimensions of the unit cell. During the second we have been concerned with the arrangement of the cell elements in the cell. We have gone far past the point we were able to reach by our older methods ; the measurement of crystal angles was sufficient only for partial progress along the first stage, and for little or none along the second.

CHAPTER V

SOME COMPLEX CRYSTALS

The third and last stage of the analysis of a crystal structure, viz. the determination of the positions of the atoms in the cell-element, is always the most difficult ; in the present state of our knowledge we are often unable to complete it. As we have already said, the full story is written in the photographs and spectrometer readings, but our skill is insufficient for the interpretation of all that is contained therein. We are glad to make use of any other aids that are available, of which indeed there are several, and we may well consider some of them.

In the first place, it is obvious that we may expect guidance from chemical considerations. Though the chemical formula of a molecule is derived from its behaviour within a gas or a liquid, and though it is often written down as a guide to the details of composition rather than as a description of the relative positions of the component atoms, it nevertheless gives valuable indications of position, even when the molecule is built into the crystal. The results of X-ray analysis show often that the chemists have under-estimated the value of their formulae in this respect. 'They builded better than they knew.' Consequently, there is a tendency for the X-ray analyst to lean on the chemical formula, especially when his present skill does not enable him to reach his goal unaided.

Another source of invaluable help has been found in the discovery of a certain constancy in the sizes of the atoms. An atom is not to be thought of as occupying a spherical domain of constant size to the exclusion of other atoms of the structure. We are justified only in saying that an atom in a given electrical condition will oppose such an entry with

a repulsive force which begins to rise quickly and to a high value at a certain stage of the mutual approach. For instance, the figures in the following table give the ' radii ' of certain atoms when built into ionic structures :

O^{--} 1·32	F^{-} 1·33	Na^{+} 1·01	Mg^{++} 0·75
S^{--} 1·69	Cl^{-} 1·72	K^{+} 1·30	Ca^{++} 1·02
	Br^{-} 1·92	Rb^{+} 1·50	Si^{++} 1·20
	I^{-} 2·19	Cs^{+} 1·75	Ba^{++} 1·40.

Each negative or positive sign means, respectively, the addition or subtraction of an electron. Thus, in rocksalt, the distance between the negatively charged chlorine and the positively charged sodium is $1{\cdot}72 + 1{\cdot}01 = 2{\cdot}83$. We have already seen that the distance between the carbon atoms in the non-ionised crystal diamond is 1·54, and in graphite, also non-ionised, is 1·42. We shall give special consideration to the carbon atom when we come to the structures of organic crystals.

These values of atomic radii are derived from structures that have been analysed by X-rays : they are often used in projecting the atomic arrangements in structures new to analysis. It is very striking to observe, in such a case, how closely the first approximation, obtained by packing together an assemblage with the dimensions of atomic domains as given in the table, corresponds with the final structure attained by careful consideration of the intensities of reflection. A very large number of crystal structures are not ionic, however, and to these the figures of the table cannot be applied. It is interesting to observe that calculations of the sizes of atomic radii which are based on the principles of the modern wave-mechanics appear to be in fair agreement with the experimental values given in the table.

From yet another direction we may reasonably expect help, viz. in the development of general rules relating to the mutual arrangements of atoms and molecules in various types of crystal : rules which have not been fully stated before because they relate particularly to features of the solid which have hitherto been unknown or known only in

part. A remarkable illustration of what may be looked for in this direction is the discovery of the part played by the oxygen atoms in many compounds, and particularly in the silicates. These are very complex substances, and were it not for the discovery of the rule in question their analysis would not have reached its present advanced stage.

It is, therefore, worth while to give a little time to the consideration of the silicates and their kindred. Their universal occurrence and their importance make them all the more interesting. Moreover, while we do this, we have an opportunity of examining the effect of a certain principle, which we may call the 'enhancement principle,' on the intensities of the reflections from selected sets of planes. It is based on the simultaneous existence of two periodicities in the crystal, which may or may not be commensurable. We shall find it of value in the study of organic crystals also.

It is estimated that oxygen, silicon, aluminium and iron by themselves compose about 87 per cent. of the earth's crust, and if we add four other elements, calcium, sodium, potassium and magnesium, only about 2 per cent. is left for all the elements that remain. Oxygen itself is about half the whole crust. Now the named elements are those of which the silicates are mainly built.

Not only are the oxygen atoms the most numerous, but they behave as if they were the most bulky of the atoms of which the silicates are composed, so that on account of their predominant size and number the other atoms are found to conform to certain simple and characteristic arrangements of the oxygen atoms which occur again and again as an underlying *motif* in all the silicates yet analysed. The most simple and complete of these arrangements is that which we describe as the close packed arrangement of oxygens, considered to be spheres : an arrangement which may, of course, be cubic or hexagonal. The distance from centre to centre is about 2·7 A.U. In such a grouping there are two kinds of interstices : in one case a space is included by four oxygen atoms, and in the other included by six, as illustrated in

Fig. 72. In the interstices are found the silicon or metal atoms. Some of the elements mentioned above appear to fit comfortably into the interstices, but calcium, sodium and

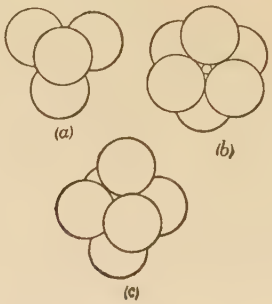


Fig. 72.

potassium are rather too large to do so, and break up the simplicity of the structure without, in many cases, disturbing its general arrangement (Fig. 73). Let us take one or two examples.

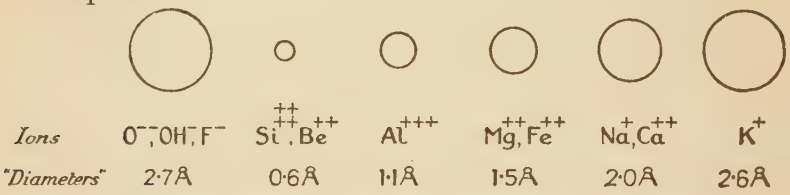


Fig. 73.—Relative sizes of the more common constituents of the silicates. W. Lawrence Bragg and J. West, *Proc. Roy. Soc.*, 114, p. 450.

The simplest of all the structures built on this system is that of beryllium oxide, of which the plan is shown in Fig. 74. There are equal numbers of beryllium and oxygen atoms, which all fit into holes between four oxygens without forcing the oxygens apart. The figure shows two successive layers.

Next in simplicity is perhaps corundum, which when coloured by a slight admixture of a foreign substance becomes ruby or sapphire, Al_2O_3.

The spinel group, including magnetite, is based directly on the cubic close packing. Into the tetrahedral interstices may go divalent atoms, magnesium, zinc and iron in one of its forms : into the others, the trivalent, such as aluminium,

chromium or iron in another of its forms. Not all the interstices are filled ; the valencies of the oxygens have to be balanced by an equal number of valencies of the opposite

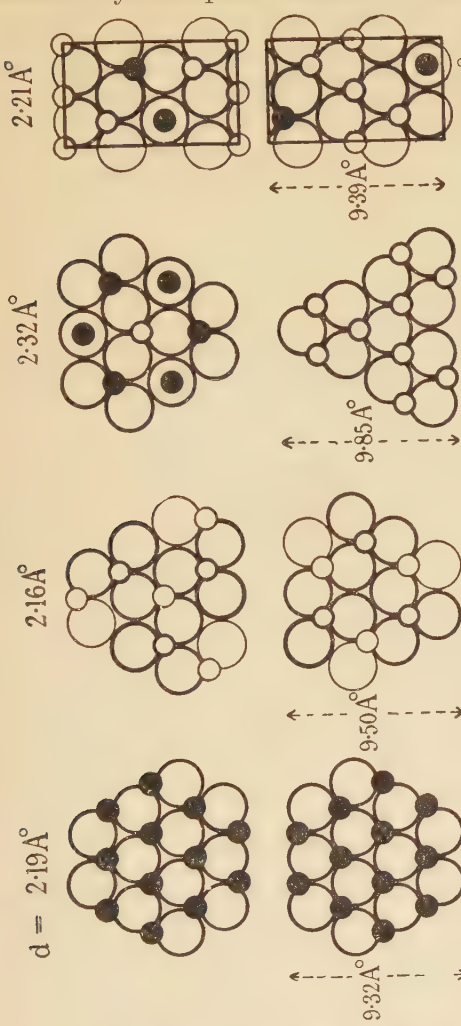


FIG. 74.—Plan of the structures of beryllium oxide, corundum or ruby, spinel and chrysoberyl. W. Lawrence Bragg and G. B. Brown, *Proc. Roy. Soc.*, 110, p. 34.

kind, and this sets a limit to the number of the other atoms. The latter are arranged in a definite pattern, the unit cell containing the substance of two molecules.

The silicates are more complicated : let us first consider the substance disthene or cyanite, Al_2SiO_5. This also is founded on cubic close packing of oxygen atoms, but the simplicity of the oxygen arrangement is completely masked by the other atoms which are inserted into the interstices between the oxygens. The insertions are made according to a regular pattern, and necessarily its scale is much larger than

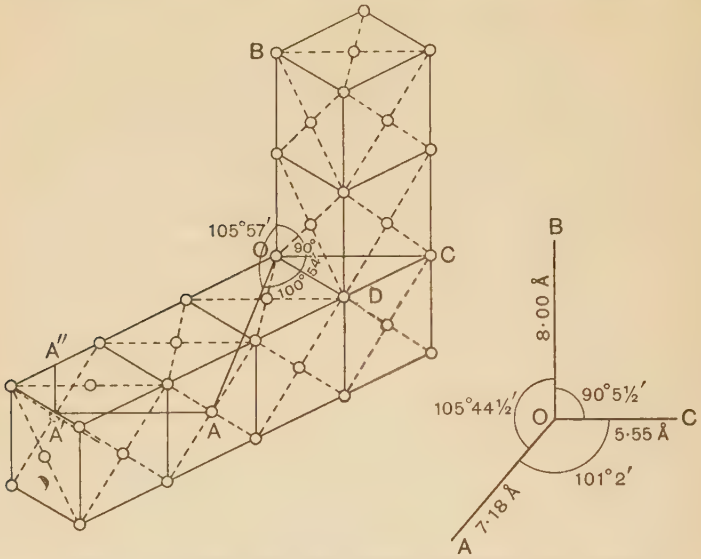


FIG. 75.—Diagram to explain the structure of disthene. W. Lawrence Bragg and J. West, *Proc. Roy. Soc.*, 114, p. 450.

that of the simple oxygen pattern. In fact, the unit cell is found to contain four elements, each of them consisting of one molecule : so that there are in the cell eight aluminium atoms, four silicons and twenty oxygens. This larger cell is carved out of the oxygen structure in a very curious way : there must, of course, be something remarkable about its form since it has to contain twenty oxygen atoms and at the same time its corners have to coincide with corners of the nearly regular oxygen lattice. In Fig. 75 (left) is drawn a portion of a face centred lattice. Consider the parallelepiped of which OA, OB and OC are three edges : the points O, A, B, C,

are all points on the lattice. The volume of the cell is the same as that of the cell of which the edges are OA', OB and OC, since AA' is parallel to OC. This again is equal in volume to the cell of which the edges are OA'', OB and OC, because $A'A''$ is parallel to OB, and again to the cell the edges of which are OA'', OB and OD, because CD is parallel to OA''. The volume is now seen to be equal to

$$OD^3 \times 2 \times 5/2 = 5OD^3 :$$

it is therefore five times the volume of one of the small cubes, each of which contains four oxygens. The length of OA, OB and OC are in the ratio $\sqrt{14}/2 : 2 : \sqrt{2}$. If the diameter of the oxygen atom is taken to be 2·70, the length of a face diagonal of one of the small cubes is 5·40. The lengths of OA, OB and OC are readily calculated to be 7·16 : 7·63 : 5·40. The angle between OB and $OC = 90°$, between OC and $OA = 100° 54'$, and between OA and $OB = 105° 57'$.

These figures are to be compared with the dimensions of the disthene cell as found by experiment : they also are set out in Fig. 75 (right), and the parallelism is obvious. It should be added that the positions of the oxygen molecules in the disthene have also been determined, and are found to be closely in agreement with those of the simple lattice. There is merely such a change in their positions as shows the existence of a slight distortion, probably due to the fact that the atoms of aluminium are rather too large for the interstices into which they are forced. The disthene cell is triclinic, having no regularity of dimensions ; but it is now clear that its form is but little removed from that of a highly symmetrical arrangement of close packed spheres. There are, in fact, two periodicities, one of them a little irregular. The large unit of pattern is repeated throughout the structure in a manner which is precisely defined by the dimensions of the unit cell. Besides this there is a much smaller pattern, that of the oxygen lattice, which is not repeated with perfect accuracy because the lattice is a little distorted. The spacings of the disthene crystal are much larger than those of the lattice on which the oxygen atoms still lie very nearly.

A rotation photograph of the crystal will, therefore, show a number of spots close to the centre of the plate, due to large spacings, which would have no parallel in a similar photograph of the oxygen lattice if it could be made.

From the construction of the crystal it is clear that any set of planes of the regular oxygen lattice very nearly includes all the points of the disthene lattice, since the points of the latter very nearly coincide with some of the points of the former. Thus every spot on a rotation photograph of the oxygen lattice coincides with a spot on a rotation photograph

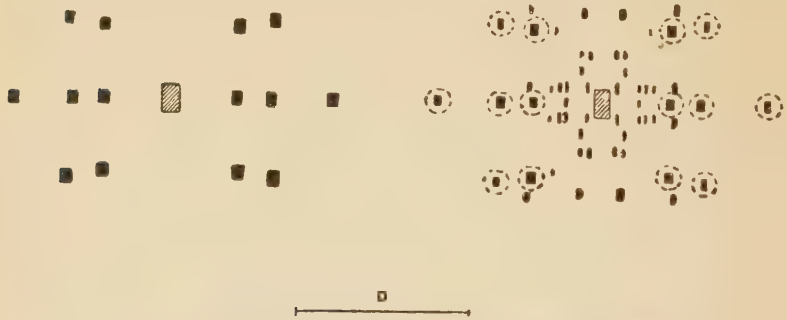


FIG. 76.—Comparison of spots of rotation photograph of disthene (right) with corresponding photograph of imaginary structure of close-packed oxygens (left). See text. The length *D* shows the distance of the axis of rotation from the photographic plate. W. Lawrence Bragg, *Nature*, 120, p. 140.

of the disthene lattice, but the reverse is not true. We should, therefore, expect to find that some of the spots of the latter photograph are enhanced because they are also oxygen spots. The effect is actually found and is very striking. Numbers of other crystals show a similar enhancement from similar causes.

Consider the drawing on the right of Fig. 76 : it is copied from a rotation photograph of disthene about the *b*-axis (*OB* of Fig. 75). On the left hand is shown a similar drawing showing what would be obtained from the rotation of the oxygen lattice of Fig. 75 about the same axis, without the silicons and aluminiums. It is, of course, an imaginary picture, since the oxygens would not hold together without the cementing atoms. An example of the way in which such

calculations are made will be found in the last chapter, in connection with an analysis of the structure of aluminium metal. The rectangular form of the spots in all the drawings is a conventional representation of the form in the actual photographs, which naturally approximated to the form of the crystal itself. The large spot in the centre of each drawing represents the spot due to the action of the direct pencil of X-rays. It is to be observed that all the spots in the figure on the left correspond to spots in the figure on the right; these latter are enclosed in circles. It will be observed, also, that the enclosed spots are very strong. In this very interesting way we obtain full confirmation of our hypothesis.

The composition of such a substance may be likened to a piece of tapestry. The oxygens correspond to the canvas with its regular arrangement of threads. On the tapestry a pattern is embroidered, the unit of which may be a parallelogram of any form; but it must so far conform to the oxygen pattern that the area of the parallelogram is an integral multiple of the area of a unit of pattern in the canvas.

Yet the analogy, though very satisfactory on the whole, is not quite complete. The wool is so soft that it conforms absolutely to the pattern of the canvas, but the metal atoms are comparatively unyielding and sometimes strain the oxygen framework, opening it out as a whole and distorting its simple angular relations. There is a slight effect of this kind in the disthene crystal, indicated by the small amount to which the lines of Fig. 75 (right) fail to conform to the corresponding lines of Fig. 75 (left).

A scale drawing of three silicates (Fig. 77) shows the way in which the auxiliary atoms are forced into the oxygen structure. All the three structures are based on a hexagonal close packing of the oxygen atoms, but whereas the first, crysoberyl, conforms closely to the simple design, the second structure, that of olivine, is expanded by the insertion of magnesium atoms, and the third, monticellite, by the further insertion of calciums. In each case the large white circles

FIG. 77.—1. Oxygen atoms lying nearly in the plane of the paper. 2. Oxygen atoms in a plane above that of the paper, included to show tetrahedral groups. 3. Oxygen atoms below the plane of the paper. 4. Ca Mg and Al atoms lying on the oxygen layer marked (1). 5. Ca Mg and Al atoms lying below the oxygen layer. 6. Si or Be atoms.

represent the oxygen atoms, one layer lying in the plane of the paper. In the first of the three the circles all touch each other ; in the second and third they are opened out more and more. One oxygen atom has been withdrawn from the layer in the plane of the paper, so as to show the layer that is below, and one added—*A*—which belongs to a layer above. Other details are described in the legend below the figure.

These complicated structures could not well have been analysed without some help from the conception of a master arrangement of oxygens.

If now we reconsider the structure of quartz itself, which has already been described, we observe that a principal feature is the tetrahedral group of oxygen atoms which includes an atom of silicon, and the distance between oxygen centres is 2·5 A.U. Tridymite and cristobalite are more regular forms of silica, the former hexagonal, the latter cubic, and in these also the tetrahedron remains. Their structures are easily described. The latter crystal resembles diamond, the carbon being replaced by silicons : between every two silicons an oxygen is placed. The former, tridymite, may be looked on as derived from hexagonal close packing just as cristobalite can be derived from cubic. In these silica structures we have no longer the close packing of oxygens, but a pattern far more open. (Gibbs, *Proc. Roy. Soc.* 113, p. 351).

These results of X-ray analysis unfold to us a plan of construction which causes us to look on the silicates in a new way. The immense variety in composition which occurs within one and the same mineral species no longer invites us, as it has done in the past, to use stupendous chemical formulae for their description and explanation. There is simply one common framework into which all sorts of patterns may be inserted. There is only one great molecule, as in diamond ; yet the composition of the molecule may vary from point to point. The grouping of atoms into separate molecules within the crystal seems to have no meaning : we have another and a far better way of describing the design.

The study of the crystals of organic substances presents

interests and difficulties of its own. It is of interest that in this case also we obtain assistance from the principle of enhancement due to the existence of coinciding periodicities. We have just been considering those crystals of which the silicates are notable examples : crystals which form the great bulk of the earth's crust. We have seen that they are built on an oxygen framework. In the organic substances, on the one hand, the carbon atom plays the principal part. These substances are, considered quantitatively, an insignificant component of the materials of the earth ; but they are of first importance because they play so great a part in the life and movement that goes on upon the earth's surface.

The composition of an organic compound is in general represented by a very complicated chemical formula : the molecule contains twenty, fifty or a hundred atoms. We may be sure that the crystal, which nearly always contains more than one molecule, will have a very complicated structure. It might be thought, therefore, that the difficulties of solution would be too great for our present knowledge and experience. And so, indeed, they would, if we were to expect to be able to put every atom in its place. But though we may rarely obtain the full solution we can always go a little way, and sometimes quite a long way towards it ; and even the partial success is of great interest and is instructive. There are certain obvious reasons why this is so. The chemist, when he assigns a formula to an organic substance, does more than name the number of atoms of each kind of which the molecule is composed. He tries to indicate the relations of the atoms to one another so far as he can. For example, he writes the formula for benzil not merely as $C_{14}H_{10}O_2$, but also as

$$C_6H_5 \,.\, CO \,.\, CO \,.\, C_6H_5 :$$

implying thereby that two benzene rings are linked together by a chain of two carbon atoms to each of which an oxygen atom has been attached. He employs this kind of description because he has found the great importance of

structure in the molecule, and wishes to express in the formula such knowledge of structure as he has succeeded in obtaining. Even in its improved form such a formula cannot show all the relations of the atoms to one another The molecule has extensions in three dimensions, and the position of each atom requires for its expression three co-ordinates of reference to some standard set of planes fixed in the molecule. The formula expresses very little of all this. The matter is obviously important, however, because it becomes more and more clear that the molecule's reactions to external influences depend on its geometrical form, on the varying aspects which are presented at various points of its surface, and on the particular character of that portion at which the reaction has the opportunity of occurring. For instance, the long molecule of a fatty acid has at one end a carboxyl group, at the other a methyl group. If a number of molecules are laid side by side to form a sheet, one side of which is a mass of carboxyl and the other a mass of methyl groups, the first face can be wetted with water, the other cannot. Sheets of this or a similar nature actually occur, for instance, in the surface of a soap bubble. The chemist has long recognised the importance of stereometry, that is to say, he has studied the spatial structure of the molecule. Now the X-rays are specially fitted to measure quantitatively the spacings and orientations of the atoms and molecules in the solid substance ; there is, therefore, strong inducement to apply the X-ray analysis to the organic substances in order to add if possible to the knowledge of stereometry already possessed. And it may be said that every fresh determination by X-ray methods of the spatial relations in the molecule confirms the chemist's first estimate of their importance.

The long chain compounds, to which classification the fatty acids belong, have already yielded results of great interest. It might be thought that their structure would be difficult to put into evidence ; and indeed single perfect crystals are rarely seen. But imperfect crystals are easily found : in fact, it is difficult not to find them when X-rays are employed in the search. Even when a molten drop of

such a substance as stearic acid is allowed to solidify upon a plate, the molecules, as the X-ray analysis shows, gather themselves together in an ordered fashion, forming thin sheets in which the molecules lie side by side and transversely to the sheets. The whole mass is not one single crystal, but fragmentary crystal flakes are jumbled together. And there is some order even in this jumble, for the flakes tend to parallelism with the surface of the plate, especially if a rubbing pressure is applied.

Let us suppose that such a plate carrying a thin layer of the substance is mounted on the X-ray camera so that the plane surface contains the axis of rotation, and that the plate is oscillated through a few degrees about the position of reflection. The incident monochromatic rays are defined by slits which are parallel to the axis of the instrument. Examples of the line spectrum thus formed are shown in Figs. 78 and 80 (Plate IV), and 83 (Plate V).

The series of regularly spaced lines in each of the photographs is due to reflections of various orders by planes parallel to the surface of the flakes. The substances represented by the photographs in Fig. 78 are hydrocarbons of different length of chain, the number of carbons in each being indicated. The lines draw together as the number of carbons increases. The spacing in each case can be calculated in the usual way, and when the results are plotted, as in Fig. 79, against the number of carbon atoms in the chain, it is seen that the relation between the two quantities is represented by a straight line. This is just what we should expect if the disposition of the molecules is as stated above. The crystal is to be thought of as consisting of a number of monomolecular layers, in each of which the molecules are parallel to each other and transverse to the layer. There is nothing in these photographs to show that the chains are actually perpendicular to the layer, but it might be surmised that this is the case, and as a matter of fact there is separate X-ray evidence of it. In the case of other long chain compounds, such as the fatty acids $CH_3(CH_2)_n . CO . OH$, it was always an obvious and even likely possibility that the chains

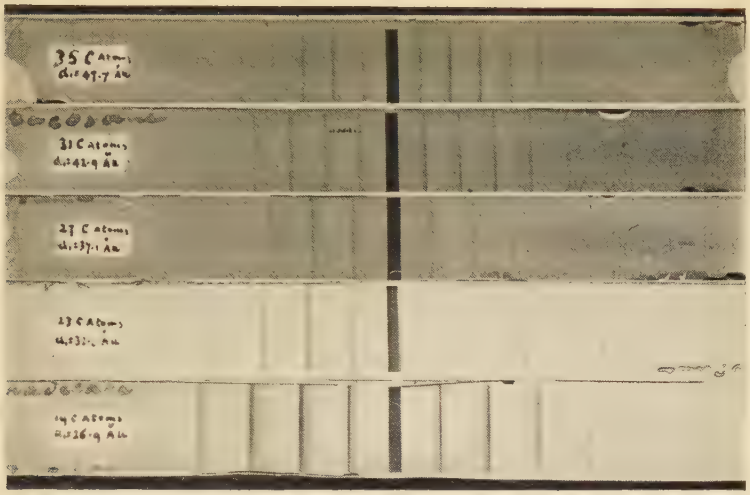
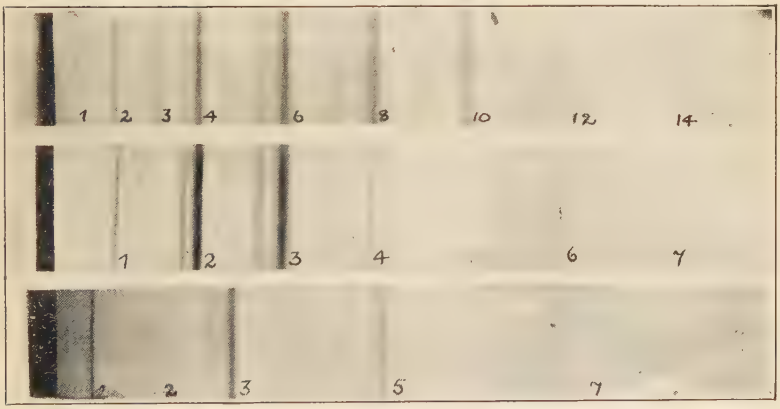


FIG. 78.—Spectra due to various hydrocarbons in which there are respectively 35, 31, 27 23 and 19 carbon atoms respectively (Müller and Saville.)



Spectra due to ketones (Shearer). (See p. 132.)

Top (80*a*). A methyl ketone.
Middle (80*b*). Ketone oxygen at one-fifth of the chain length.
Bottom (80*c*). Ketone oxygen at the centre of the chain.

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might be oblique to the layers, because with such a composition there might well be lack of symmetry across the axis of the molecule. It has recently been found possible to obtain perfect separate crystals of the acids, with which a far more thorough investigation of structure can be made, and the oblique position of the chains has been demonstrated.

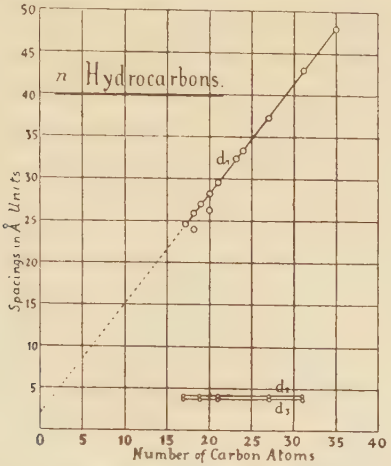


FIG. 79.—Diagram (Müller and Saville) showing the increase in the long spacing of hydrocarbons as the number of carbon atoms is increased. Two spots of the line are due to alternative forms. The d_2 and d_3 are 'side spacings' (see p. 135), and are the same for all the substances.

For the moment we put aside these measurements with the single crystal in order to consider certain simple but important measurements which can be made on the less perfect material.

In the hydrocarbon spectra of Fig. 78 the intensities of the various orders decrease regularly from the lower to the higher. But in the case of the fatty acids, Fig. 83, the even orders are far weaker than the odd on the whole; and, in general, abnormalities of one kind or another are found in the spectra of almost all the long chain compounds. The explanation of these effects is very interesting, and, moreover, opens the way to the determination of the positions of attached atoms and groups of atoms on the carbon chain: such as, for example, the point of attachment of a ketone oxygen.

Let us go back to first principles. If in Fig. 8, $p, p, p \ldots$ represent layers which can scatter a fraction of the X-ray beam that traverses them, while permitting the passage of the rest, there is a measurable reflection of the X-rays provided that, as we have seen, the law $n\lambda = 2d \sin \theta$ is fulfilled, where d is the shortest distance from layer to layer.

Reflection will occur at the same angle if we invert the structure, making the layers into empty spaces and the empty spaces into layers. In Fig. 81(a) the shaded areas represent material which uniformly scatter the X-rays, and the white intervals represent spaces which scatter less than the rest or not at all. This is analogous to the well-known principle of the optical diffraction grating : spectra of the same character and in the same position are found no matter whether the grating consists of black lines on a white ground or white lines on a black ground.

Suppose now that new blanks were formed in the material, as in Fig. 81(b), interleaving exactly those that were there before. The spacing has been halved : the corresponding values of sin θ are therefore twice as great. In other words, the odd orders of the (a) spectra have disappeared. The spectra of (b) are only the even spectra of (a).

If the new spaces were not entirely blank, but were less full of scattering matter than the main body, as at c, we get a compromise between the spectra of a and b : there will be spectra in all the positions of the a spectra, but the odd orders will be weak as compared with the even. This is actually the case of the (111) planes of NaCl, as we have seen before.

What then will happen if we insert into a not new spaces which scatter less than the average but slabs which scatter *more* ? What sort of spectra will be obtained from the substance represented by d ? It is easy to conceive, and in fact easy to prove mathematically, that as we raise the density of the scattering matter in the new spaces we strengthen the odd orders as compared with the even : we have the exact antithesis of the first case in which as we

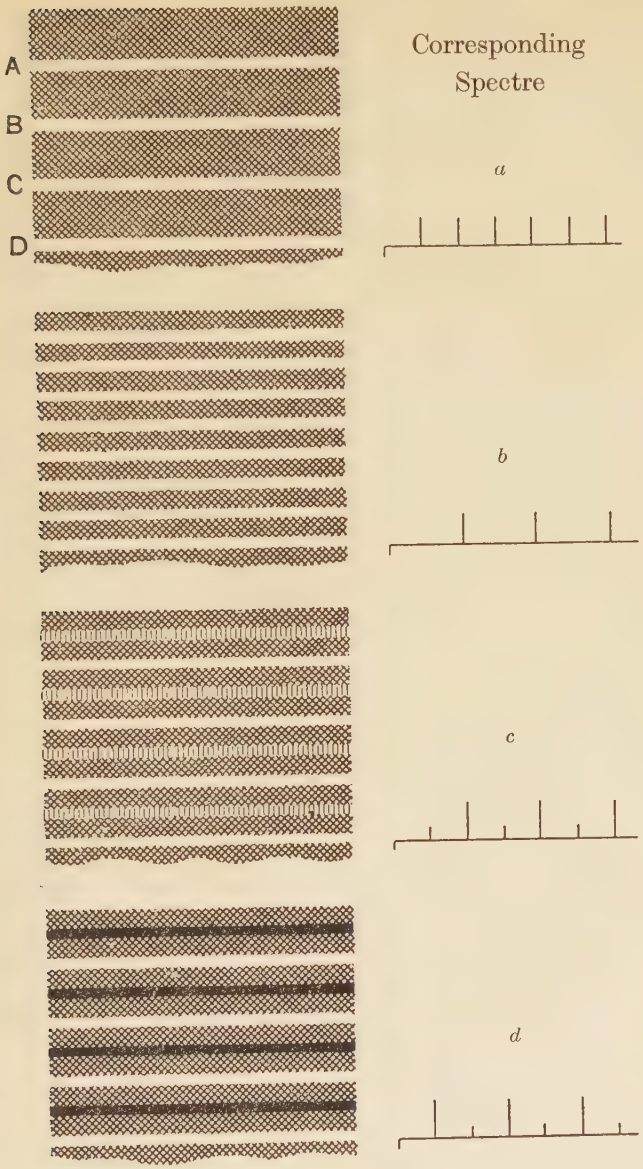


FIG. 81.

diminish the density in the new spaces the odd orders tend to disappear.

Let us apply these conclusions to our photographs of the long chain compounds. The hydrocarbons show a smooth decrease in the intensity of their spectra : it is natural to suppose that they can be represented by Fig. 81(*a*). The shaded areas represent the main bodies of the molecules, and therefore a fairly even distribution of carbon atoms : the white spaces represent deficiencies in scattering power, such as may be expected because there are methyl (CH_3) groups at the ends of the chains which take up space and yet do not scatter X-rays so well as the body of the chain. The fatty acid spectra are, however, like those due to Fig. 81(*d*) ; and we must, therefore, suppose that this figure more nearly than Fig. 81(*b*) represents the arrangement of scattering matter in the crystal layer. It is easy to understand how this may arise, because the carboxyl ends of the long chains have a strong attraction for each other, and there must be a tendency to form pairs of double length. The methyl groups, as in the hydrocarbon, occupy a space which corresponds to the blank of Fig. 81(*d*), whereas the carboxyl groups can form a sheet of extra density. If we suppose that the excess of scattering material in one place is equal to the defect in the other the odd orders will disappear entirely.

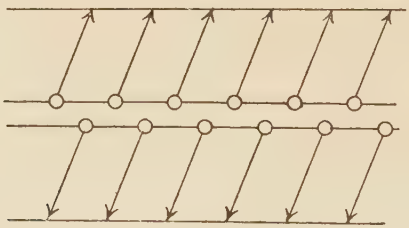


FIG. 82.

Instead of speaking of two molecules end to end it would be more correct to say that double layers will be formed, the two outer surfaces of which would show only methyl groups, while the carboxyl groups would be locked together in the interior as represented by Fig. 82. The ' staggered '

effect is introduced into the figure as a possibility, which might, indeed, extend to two dimensions, and not only to the one which is all that the diagram shows. That is to say, each carboxyl group in one of the 'sub-layers' may be linked to several neighbours in the other. Such an arrangement seems to be extremely common in crystalline structures and might reasonably be expected, for there must be links to hold the whole together. A double layer of this kind is a first step towards the complete crystal: the completion would require the addition of layer to layer in proper orientation. The well-known 'black spot' of the soap-bubble consists of a layered arrangement which at its thinnest, when there is but one layer, has a thickness equal to that of the sodium oleate spacing, as measured by X-rays. Both faces of the film present methyl groups to the surrounding air; in the centre of the film is a layer of carboxyl groups.

Confirmation of this view of the fatty acid structure is obtained when we compare the spacing of stearic acid with that of octodecane which has a similar number of links in its chain. The former is 43·65 A.U., the latter is 25·9 A.U. Now, if all the 18 carbon atoms were put in a straight line, the length of the chain so formed would be about 28, assuming 1·54 to be the distance from centre to centre of two neighbouring carbon atoms as in diamond. This is a little too much for the length of octodecane, especially as allowance has to be made for the methyl group at each end, but that may well be because the carbon atoms are not lying in one straight line, but in a zig-zag pattern. The increase in length for each two carbon atoms has been measured for a number of hydrocarbons containing from 17 to 35 carbon atoms: it is very nearly 2·6 A.U. The distance between one carbon atom of the diamond and the next but one in any direction is 2·51; and this suggests strongly that the linkages of diamond and the hydrocarbon are the same in character.

We can, therefore, give a ready explanation of the length of the hydrocarbon chain; but clearly the stearic acid spacing is far too large to be covered by a single molecule. Two are required to bridge the interval: as we shall see in a moment

they do so in a slanting fashion, which in a large measure explains why the spacing of stearic acid is less than twice that of octodecane.

We are now in the position to extend the argument illustrated by Fig. 81, and thereby to arrive at another result of interest. If we had inserted a new blank space into each shaded area of Fig. 81 (*a*), not in the middle as in Fig. 81 (*b*), but one-third of the way across, the corresponding spectrum would show intensification of the third, sixth, ninth . . . orders. If the new space were one-quarter of the way across from one of the old spaces to the next, the fourth, eight . . . orders would be strong ; and so on. Conversely, if matter is added in these positions, and that which is added is equal to the defect in the blank spaces, the orders in question will entirely disappear.

It is found that if a ketone oxygen is added to the centre of a hydrocarbon chain the even orders of spectra all disappear, as shown in Fig. 80*c*. If it is added one-fifth of the way along, the fifth order goes out as in Fig. 80*b*; and, generally, the anticipation of the previous paragraph is entirely verified. The photograph of Fig. 80*a* has a special interest : it represents a methyl ketone, a chain in which the ketone oxygen is attached to a carbon which is only separated from the end of the molecule by the CH_3 group. Since the oxygen is so near one end the disappearing order must be far along the spectrum, and the photograph is already consistent with that expectation. But a fresh effect comes in : new lines appear halfway between the old. It is clear that the fatty acid structure is being adopted : the ketone oxygen is so near the end of the chain that it exercises an effect on the corresponding end of another chain, and the double length once more appears. These results are due to G. B. Shearer.

We have here in effect a very delicate balance in which we can compare the weight of an attached group with the deficiency in weight of the methyl group, and, not only so, we can also find the point along the chain where the attachment has been made.

So far we have found the imperfectly crystalline mass to

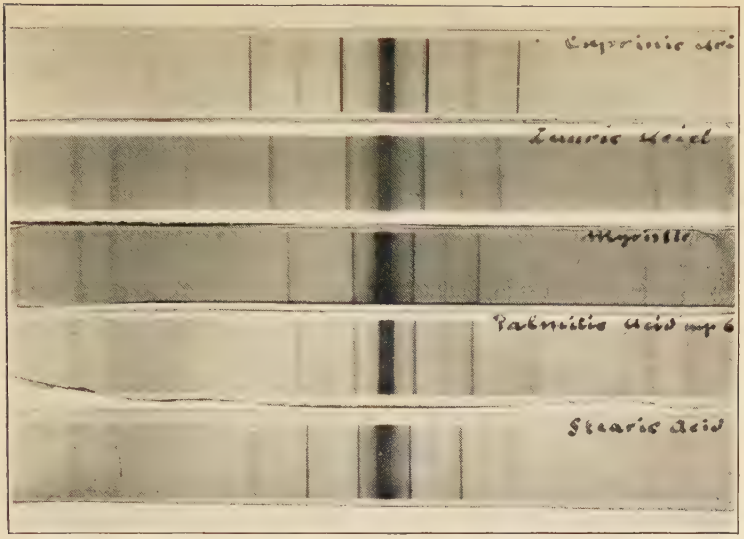


FIG. 83.—Spectra due to various fatty acids. (Müller, Trans. Chem. Soc. 123. p. 2043.)

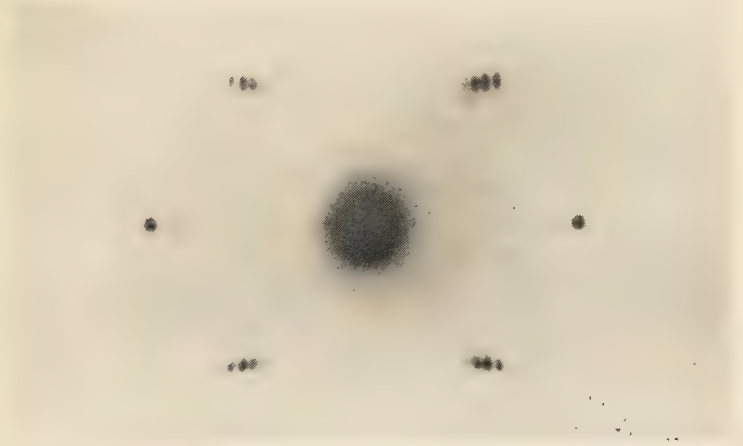
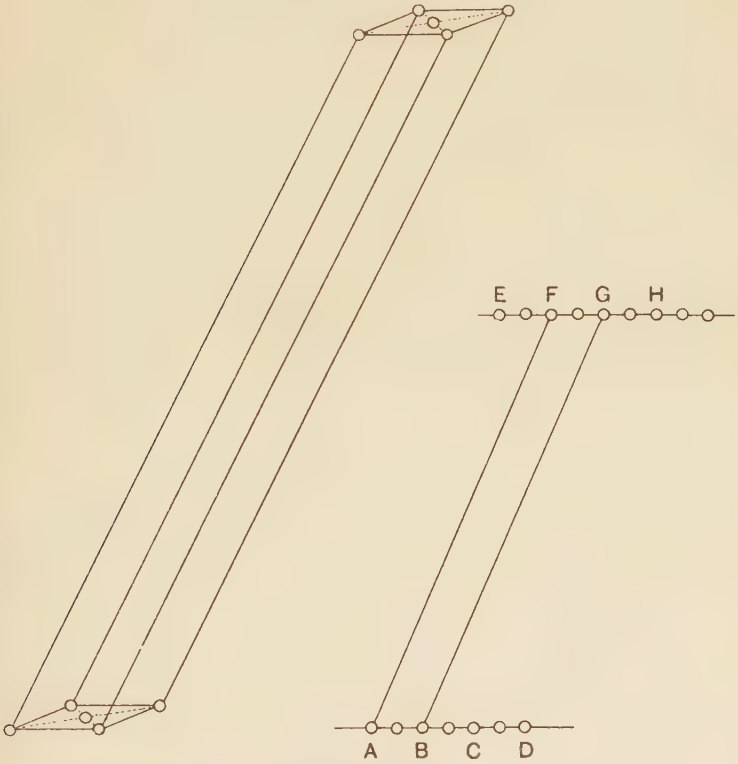


FIG. 85*a*.—Rotation photograph of stearic acid about the *a*-axis. (Müller.)

be sufficient for our purpose. But, as always, a single crystal if it can be obtained is infinitely to be preferred. A large number of long chain compounds have been examined by the methods described above. More recently it has been found possible to obtain perfect crystals in one or two cases : stearic acid is one of them. The single crystal being available it is readily shown that the unit cell of stearic acid has the dimensions :

$$a = 5{\cdot}546\ ;\ b = 7{\cdot}381\ ;\ c = 48{\cdot}84\ ;\ \beta = 63^\circ\ 38'.$$



(*a*) FIG. 84.—Stearic acid. (*b*)

The form of the cell is represented in Fig. 84*a*, and the arrangement is of the monoclinic prismatic type which has already been described on p. 107. The specific gravity of the

substance being known, it can be calculated that the unit cell contains the substance of four molecules. As already explained the symmetry of the cell must be realised by the presence of four elements which we have called *A*, *B*, *C* and *D*. We make the assumption that in this case the four elements are the four molecules. The four molecules can be divided into two pairs each having a centre of symmetry. If one pair is placed so that its centre of symmetry is at each corner of the cell in the drawing, the other pair can be derived from it either by reflection across the *ac* plane or a rotation of 180° round the *b*-axis, followed by a shift which translates the centre of the molecule from the corner of an *ab* face to the middle of that face, the molecule retaining its orientation during the move.

The choice of the angle of the cell is made on consideration of the intensities of the reflected spots on the rotation photographs. Suppose that Fig. 84*b* represents the projection of the centres of the pairs already mentioned upon the plane of symmetry of the crystal, that is to say, the *ac* plane. The points with letters attached are projections of one lot of pairs : the unlettered points are projections of the other. Let *AB* be chosen as the *a* axis. Then any line *AE*, *AF*, *AG*, etc., may be chosen as axis of *c* ; that which has been chosen so as to give the cell dimensions quoted above is *AF*, so that *FAB* is the angle β and has the given value.

Now we should expect that, if the *c* axis has been chosen as we should wish it to be, so that it is nearly parallel to the length of the chain, strongly reflecting planes will be found of the form (*hk*0), because such planes will include the chain. There are, for example, four very strong spots on the photograph which is reproduced in Fig. 85*a* ; the axis of rotation is the *a* axis of the chosen cell of Fig. 84*a*. The strength of the four reflections is so great that other spots barely appeared in the time allowed for the exposure. These are due to the planes which are denoted by (111), (110), ($11\bar{1}$), (020) when the cell in Fig. 84 is chosen as the unit cell. The spacings of these planes are 4·25, 4·12, 3·96, 3·70 respectively. No other choice of axes gives such simple or sym-

metrical designations to these strongly reflecting planes. The fact that (020) is so strong—there cannot on this arrangement be a (010) plane—implies that the chains lie closely parallel to the plane of symmetry of the crystal, which is itself parallel to (010) or *ac*. The fact that the three strong planes are symmetrically designated (111), (110), (111) shows that the middle one must contain the chain, while the others nearly do so. The photograph reproduced in Fig. 85*a* (Plate V) is a rotation photograph about the *a* axis.

In the photographs of hydrocarbon, already referred to

FIG. 85 (*c*).—Drawing of rotation photograph of $C_{29}H_{60}$ about the *c*-axis. From a photograph due to A. Müller.

(Fig. 79), certain rather ill-marked but strong lines are found at some distance from the centre, and occupy the same positions on all the plates, no matter what the length of the chain may be. Clearly these must be due to planes which are parallel or nearly so to the length of the chain, their spacings which average about 4 A.U. being determined by the chain's lateral dimensions. This is now confirmed by the results of the single crystal: it is these in fact that give the strongest reflections of all.

We now come to a very remarkable feature of these rotation photographs of the single crystal of a long chain compound. Let us take another example from Müller's work on stearic acid, shown in Fig. 85*b* (Plate VI). The axis of rotation is the *b* axis of the chosen unit cell. Isolated spots and groups of spots appear in the photograph. Not all of these are due to sets of planes designated by small numbers and the exceptions are principally the following, of which the first two are indicated in the reproduction :

$(2, 0, \bar{1}\bar{9})$, (2, 0, 38), (0, 1, 20), (0, 2, 19), (0, 0, 18), (0, 0, 20).

There is an obvious peculiarity in these numbers. The last figure is either 19, or near to 19, or a multiple of 19. The fact is that we have again, as we had formerly in the case of the silicates, an intensification of certain reflections, because two periodicities nearly coincide. The similarity is not complete however : there is a difference which is important and interesting. Let us approach this new case from its appropriate point of view.

Fig. 86 represents the fact that the (*hkl*) planes divide the *c* axis into *b* parts. If there is any scattering matter lying along the axis which has maxima at the points where the planes intersect it the reflection must clearly be strengthened correspondingly. There need not be a maximum at every intersection : they might, for example, be irregularly distributed as at 1, 2, and 4, omitting 3 and 5. Suppose there was in stearic acid a distribution of matter along the *c* axis which had a periodicity equal to one-nineteenth part of the axis, planes such as those set down above would then give especially strong reflections. The length of the axis is 48·84 : the nineteenth part is 2·57. This is very close to the distance between two atoms which are next but one to each other in the diamond structure, viz. 2·52. We may certainly take this

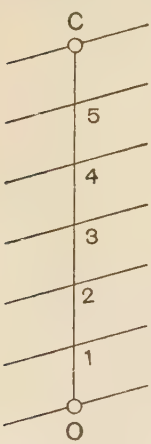


FIG. 86.

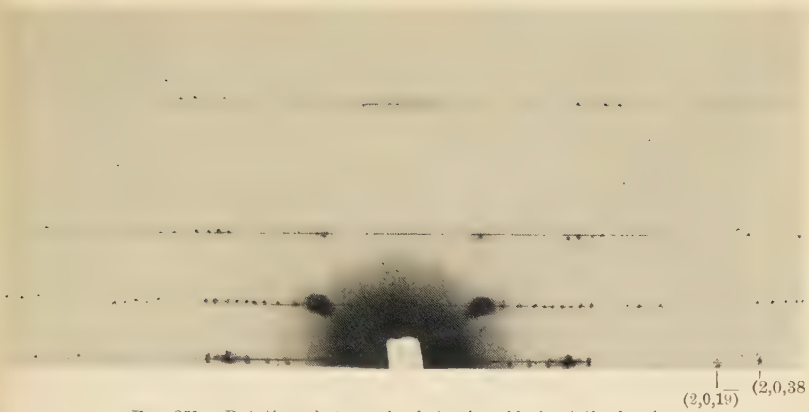


FIG. 85*b*.—Rotation photograph of stearic acid about the *b*-axis.
(Müller, Proc. Roy. Soc. 114, Pl. 39.)

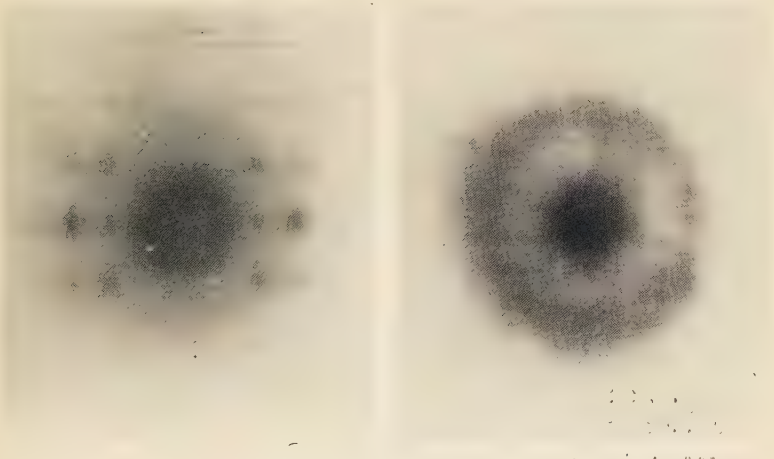


FIG. 88.—Photographs of rubber stretched (left) and unstretched (right).
(Clark.)

as confirmation of the zig-zag structure of the chain, in fact there is here an extremely accurate measurement of its periodic spacing.

Another beautiful example also due to Müller is reproduced in Fig. 85*c*. A single crystal of a hydrocarbon $C_{29}H_{60}$ is rotated about the *c* axis. It will be observed that the equator and one or two layer lines near the equator are shown by several spots. But no other layer lines appear until we come to one which is actually the thirtieth : and this is well represented. The periodicity of the carbon atoms along the *c* axis is really one-thirtieth of the periodicity of the principal pattern along the same axis.

In the case of the silicates the periodicity of the oxygen lattice extended through the whole crystal, and the larger pattern which was embroidered on it was necessarily commensurate with the smaller. In this case the periodicity of the carbon chain does not extend through space : there are gaps in it at the ends of the chain. It is enough that the periodicity has only a limited range within each cell.

The enhancement of spots where two periodicities coincide is found in other crystals and is very useful in the determination of structure.

The unit cells of naphthalene and anthracene are represented in Fig. 70. It will be observed that the values of a, b and β are almost the same in the two cases, but that the *c* axis of anthracene is longer than the *c*-axis of naphthalene by 2·52. The arrangement is exactly the same as in the case of stearic acid, except that here the molecule has already a centre of symmetry ; whereas in the case of the acid two molecules had to be put together to obtain a centre. There are now two molecules in the unit cell : in the former case there were four. The centres of the molecules are as shown in the figure, the arrangement being in both cases that which is known in crystallography as C^5_{2h}.

The directions and proportions of the axes are those which have been chosen by the crystallographer in order that the principal faces may have simple designations. The faces most frequently found on the crystal are (001) and (110), less

frequently $(20\bar{1})$, $(11\bar{1})$. Any other set of axes would have made the numbers less simple.

The results of the X-ray analysis agree with the indications of the faces. The planes that give the strongest reflections are denoted by the most simple designations, such as (001), (200), (110), $(20\bar{1})$, and so on. Also a comparison of the cell dimensions in the two cases suggests at once that the molecule is parallel to the *c* axis. The main difference between the two molecules is that one of them contains two benzene rings, the other three, and there should, therefore, be a difference in length, which, if we assume that carbon atoms are spaced as in diamond, should be about 2·52. Now this is almost exactly the difference between the lengths of the *c* axis of the two cells : and at the same time the other dimensions are very nearly in equality.

Although in this case the periodicity along the *c* axis is far less marked than in the case of stearic acid, since we have here only one or two repetitions instead of eighteen, yet it can be shown that here also there is a clear enhancement of certain spots due to a coincidence of periodicities. The molecule of anthracene shows a certain periodicity of 2·52, and within that again a half periodicity of 1·26 ; assuming that the carbon atoms are spaced as in diamond. Now

$$11{\cdot}18/2{\cdot}52 = 4{\cdot}4 \quad \text{and} \quad 11{\cdot}18/1{\cdot}26 = 8{\cdot}8.$$

Any set of planes that divides the *c* axis into four or five parts, or into nine parts, ought to have a chance of enhancement. Not every such set will actually show the effect, because the maxima are not strung along the *c* axis like so many beads ; they are not on the actual points of intersection of the planes and the axis. But on the average planes of the form (*hk*4), (*hk*5), (*hk*9) will be strongly reflecting if our hypothesis is correct. A special analysis of this kind requires that the reflections of a large number of planes shall be observed, and the results tabulated. The result for anthracene is given in Fig. 87. The curve in this figure shows the relation between two quantities, one of them the value of *l* in (*hkl*), and the other a number obtained by

giving to each plane a value 1, 2, 3, 4 or 5, according to the strength of its reflection and adding all such values together for those planes having a given value of l. About 130 different sets of planes were observed for the purpose of this comparison. There is, as anticipated, a pronounced enhancement of reflection when l is nearly equal to 4, and again when it is nearly equal to 9. We actually find the kind of effect we should expect, supposing the molecule to have the

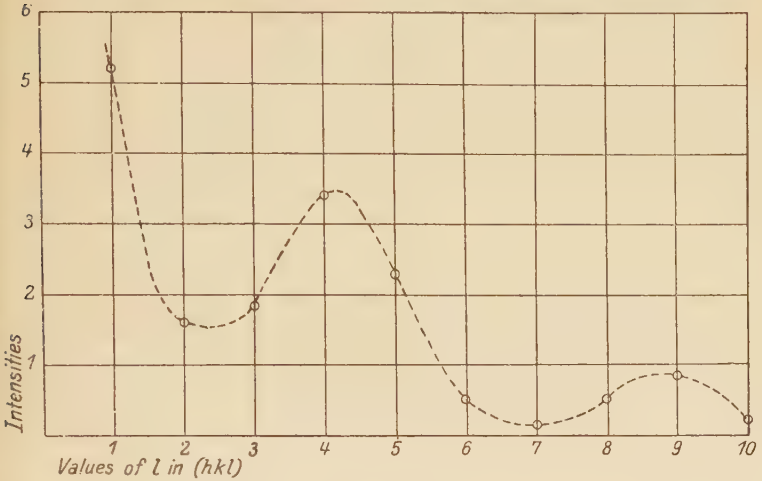


FIG. 87.

assumed shape and to be placed in the crystal so that its centre line lies along the c axis.

There is a certain resemblance between the structure of anthracene, naphthalene and the long chain compounds : in all of them the molecules lie transverse, though not generally perpendicular to the principal cleavage plane of the crystal. Their side to side attachments are stronger than those that are end to end, and because this is so the flakes are easily separated from one another in the act of cleavage, and can readily slide over one another so that the substances have the well-known greasy feeling. The lubricating quality of greases is due, as in the case of graphite, to the formation of flakes which, tough in themselves, slide easily over one another.

A number of organic structures have been examined in addition to those to which we have referred, such as tartaric acid, illustrating the connection between pattern and optical properties ; basic beryllium acetate and other similar substances, supplying good instances of the co-ordination principle ; various polyoxymethelenes which have the general character already described as typical of long chain compounds ; fumaric acid which, like several other substances, has more molecules in the unit cell than symmetry requires, thus showing that two or more (in this case three) molecules form an asymmetric group in the structure ; and so on. One of the most interesting features in all cases is the preservation of the molecule's individuality. Unlike rocksalt, in which the sodium and chlorine atoms are not obviously paired into molecules, or diamond, in which the whole crystal may be said to be one molecule, the organic substance keeps its molecules separate and distinct. The density of the crystal is low ; there is no ' close packing.' Rather, the structure is to be likened to lacework in space : the bonds which join molecule to molecule are localised at definite points of the molecular configuration. If a metal like aluminium can be compared to a pile of shot, an organic substance resembles rather an open girder structure.

The two organic substances, cellulose and rubber, have naturally drawn the attention of several workers, on account of their great industrial importance, and the value of any information as to their structure.

Under the X-rays, fibres such as ramie, cotton and wool give a photograph showing quite a number of spots : they obviously contain something that is crystalline. As the same arrangement of spots is found in so many substances of which cellulose is a common and important constituent it is to be supposed that the photograph is produced by the cellulose structure. In the making of the photograph the fibres are placed at right angles to a pencil of monochromatic rays, and the form of the result implies that the crystals are arranged in ' fibre structure.' One particular direction in the lattice of each crystal is parallel to the length of the

material, there being otherwise no limitation as to the orientation of the crystal ; and the photograph is therefore of the kind obtained by the rotation of a crystal about an axis. The number and precision of the spots are barely sufficient for an accurate determination of the size of the cell and of the position of the molecules. It seems clear, however, that the number of molecules is small ; and there is great interest in the discussion as to whether all the properties of cellulose are to be found in so narrow a compass or whether this is but an element of a larger pattern. It is always a possibility, at any rate when well defined pictures are not to be obtained, that faint lines on spots lying close to the centre, and therefore implying long spacings, may be lost in comparison with strong spots due to a more obvious periodicity. A poor photograph of a silicate, for example, may show only the pattern of the oxygen bodyground, or that of stearic acid the strong spots due to those planes of the crystal which happen to coincide with a periodicity of the carbon chain.

The cellulose photograph changes under certain treatments of the material, and such effects are studied as an aid to the understanding of what happens to cellulose in the processes of manufacture.

The results of the examination of rubber are extraordinary. Unstretched rubber shows ill-marked rings under monochromatic rays, implying the existence of a somewhat vague and unoriented periodicity (Fig. 88). Rubber when sufficiently stretched has quite a good 'rotation' photograph. Crystallisation has in some way set in during the stretching. The effect is curiously reversible : when the rubber is allowed to return to its normal unstretched condition the spot photograph is replaced by the diffuse ring. The spots do not change position as the stretching is proceeded with, nor do they increase in sharpness ; the change is of intensity only. The spots do not appear until the length of the rubber has been nearly doubled, and in the case of vulcanised rubber more than trebled. It is at its best when after an elongation of several hundred per cent. the material is on the point of breaking.

The interpretation of these observations is interesting. Any gradual change in the position of spots would imply that the periodicity was altering as the stretching proceeded : it is clear that the elements of the pattern settle into their places once and for all. It is merely the amount of some definite crystalline matter that is increasing. And since the spots do not alter in definition it is probably to be inferred that the separate crystals do not grow in size during the process. The only remaining variable is the number of the crystals ; thus the general inference is that during stretching various crystals of more or less uniform size come successively into existence, each in itself a crystal of a definite and permanent structure.

It will be seen that as a result of consideration, such as these and others which would require too much space to describe, much can be done for the determination of crystal structure even of the complicated organic compounds. We cannot place every atom with the precision that is found possible in many cases of inorganic substances, but we do obtain some idea of the general disposition of the molecules and of their form. We expect to be able to do more as our experience grows. We gradually accumulate information respecting various types of crystal and various specimens of each type : out of which accumulation principles begin to form themselves, and each fresh glimpse of a generalisation strengthens the whole attack.

CHAPTER VI

METALS

The study of the crystalline state of metals is of special interest not only in its purely scientific aspect but also because of the wideness of its application to industry. It has long been known that the properties of a metal specimen, such as toughness, tenacity, hardness, conductivity, both electric and thermal, magnetic permeability and hysteresis, and so on, depend largely upon the extent of crystallisation, the nature of the crystals, their magnitude and their orientation, as well as upon the admixture of foreign crystals, the presence of impurities, and the way in which these enter into the main structure. All these conditions are the natural subjects of X-ray investigation. A considerable quantity of research has been undertaken in consequence, and already there are striking results.

In the first place, we may examine the structure of the single metal crystal. It appears that many of them are built on the simplest possible plan, simpler even than that of rocksalt. Even if we were unable to find an isolated crystal, which is a necessity if we are to resolve a complicated structure, we should still be able to solve many of the metal structures from nothing more than a powder photograph obtained by the method of Debye and Scherrer and Hull. If, for example, a fine pencil of monochromatic X-rays is passed through a thin layer of powdered aluminium, a set of rings is formed on the photographic plate (Fig. 89, Plate VII). From the ratios of the diameters of these rings we deduce that the aluminium atoms are arranged in cubic close packing, which is that of a pile of shot. For, as we shall see presently, we can calculate what sort of a ring pattern such an arrangement will give : no other arrangement will give

the same pattern, and the two patterns agree perfectly. Hence we draw our conclusion.

Let us consider this case in detail. In doing so we shall be working out an example of the powder method, and, moreover, we shall be paving the way to certain uses of the X-ray methods which are of importance in cases where metals have been subjected to mechanical and thermal treatment. We could, of course, discover the aluminium structure by the direct examination of a single crystal, employing either the ionisation spectrometer or the rotation photograph as in the case of rocksalt and other crystals already discussed; but we have here a case where the powder method is very

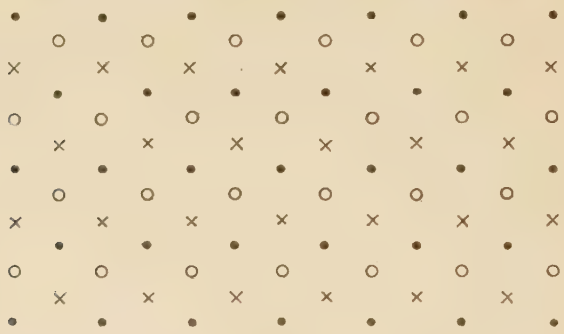


FIG. 90.

convenient and quite sufficient, and moreover the natural method to adopt in the first instance since perfect single crystals are only to be obtained by special means.

We must work out the details of the ring pattern which is characteristic of cubic close packing, and as we have not hitherto done so we must in the first place find out the form and dimensions of the unit cell in the cubic close packed arrangement.

Let us first put down a plane layer of spheres as in the figure where the points marked by dots represent the centres. Upon this we lay a second layer of spheres, the centres of which are represented by crosses and are in a plane above the plane of the diagram and parallel to it. In the diagram on the paper each cross appears at the centre of a triangle, the

vertex of which is above, that is towards the top of the page, and the base below. We now place a third layer on the second ; if the centres of the new layer are in the positions represented by the empty circles, each sphere in the new layer is related to three in the second exactly as any one in the second is to three in the first. In the diagram a circle is at the centre of a triangle formed by three crosses : the vertex of the triangle is above, the base below, as before. A fourth layer is now laid on the third : if it is to be related to the third exactly as the third to the second, and the second to the first, the new set of centres will in the figure lie over

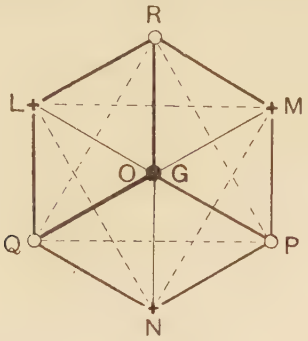


FIG. 91.

the black spots which are the centres of the first layer. Everything now repeats itself as we proceed, three layers in each repeat.

In this arrangement, therefore, every sphere is situated exactly as every other. There is another form of close packing which we will presently consider, of which the same statement cannot be made. The centres of the spheres in the former arrangement constitute a lattice, because every point represents exactly the same thing, situated in exactly the same way. If now we take one sphere from the bottom layer, three from the second, three from the third, and one from the fourth, their eight centres lie at the corner of a parallelepiped as shown in projection in Fig. 91. Since the parallelepiped encloses no other centre it is a unit cell. It

has the peculiar geometrical relation that every edge has the same length, and each face contains angles of 60° and 120°. It is the parallelepiped *GPQRLMNO* (Fig. 92) where *G* and *O* are opposite corners of a cube, and the other points are centres of cube faces. If the edge of the cube is *a*, every edge of the parallelepiped is equal to $a/\sqrt{2}$: and so also is *LN*, whence *OLN* is an equilateral triangle, and therefore the angles of the faces are of the right value.

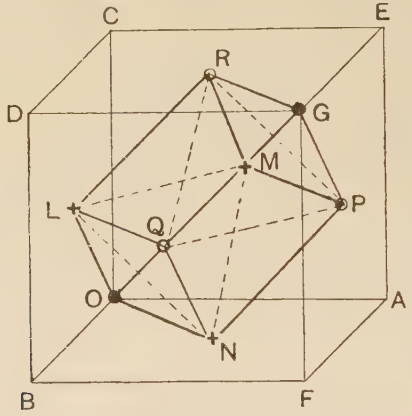


FIG. 92.

Since *O* and *L* are lattice points, so also is the point *D*, because *D* is related to *L* exactly as *L* is to *O*. All the corners of the cube are therefore lattice points, and it is possible to define the lattice as cubic, and more particularly as face centred cubic. The cube is not the unit cell, however, since four points are associated with it. The points at the eight corners belong each of them to eight cubes of which the figure shows one, and each of the points at the six-face centres belongs half to the cube in the figure and half to the next cube. The contents of the cube must, therefore, be reckoned as $1/8 \times 8 + 1/2 \times 6 = 4$. The unit cell has only one-quarter of the volume of the cube.

We have, therefore, to discover what reflections we should expect from the face-centred cube. It is convenient to consider first the reflections of a simple cube, and then to calculate the effect of adding points at the face centres.

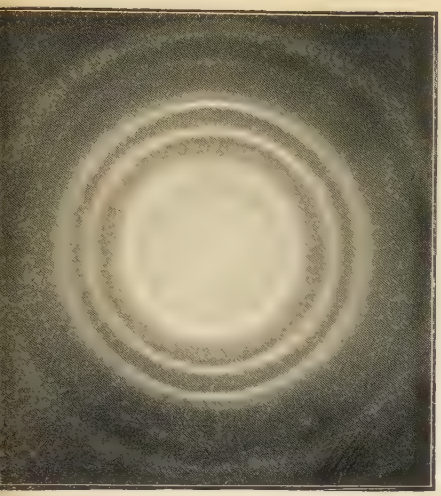


FIG. 89.—Powder photograph of aluminium. (Hull.)

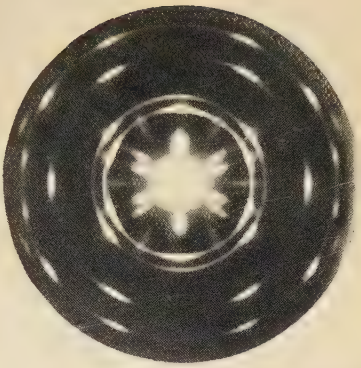


FIG. 96.—Drawn aluminium wire. (Clark.)

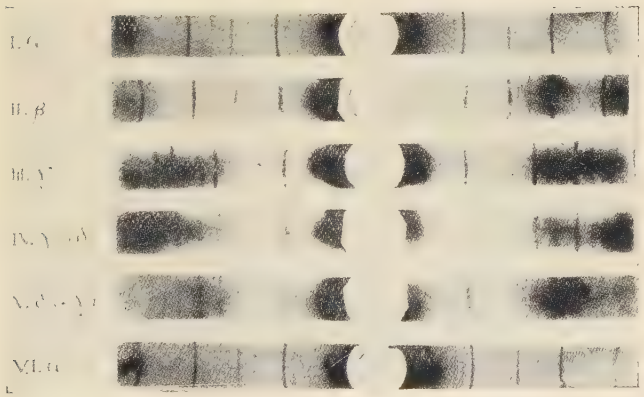


FIG. 94.—Powder photographs of iron in different modifications. The lines are portions of complete circles such as appear in full in Fig. 89. Compare with Fig. 94*a*. (Westgren.)

Planes of the (*hkl*) set have for their general equation, referred to axes *OA*, *OB*, *OC*,

$$\frac{hx}{a}+\frac{ky}{a}+\frac{lz}{a}=\text{any integer.}$$

The 'spacing' is the distance between two consecutive planes and is therefore the perpendicular from the origin which lies on the plane $hx+ky+lz=O$, upon the plane $hx+ky+lz=a$. Its value is therefore $a/\sqrt{(h^2+k^2+l^2)}$. By giving h, k, l all possible integral values we have the spacings of all the possible sets of planes belonging to the simple cube, in which *OABCDEFG* (Fig. 92) are the only representative points. These are set out in the first column of the table, and in the second column are placed the corresponding values of the spacing *d*. (See also Fig. 101.)

Spacings of Planes: Edge of Cube taken as Unity.

	Simple cube.	Body-centred cube.	Face-centred cube.
100	1·00	—	—
110	0·707	0·707	—
111	0·577	—	0·577
200	0·500	0·500	0·500
210	0·447	—	—
211	0·408	0·408	—
220	0·354	0·354	0·354
221	0·333	—	—
300	0·333	—	—
310	0·316	0·316	—
311	0·301	—	0·301
222	0·288	0·288	0·288
320	0·277	—	—
321	0·267	0·267	—
400	0·250	0·250	0·250
410	0·242	—	—
322	0·242	—	—
411	0·236	0·236	—
330	0·236	0·236	—
331	0·229	—	0·229 *

* Hull, *X-Ray Studies*, p. 189, gives a much longer list containing the spacings of some eighty planes.

If we sent monochromatic rays through a powder consisting of crystals of simple cubic structure the radii of the various rings would be given by

$$r = D \tan 2\theta,$$

where D is the distance from the crystal to the plate and θ has the values derived from the equation

$$\lambda = 2d \sin \theta.$$

Several of these rings, however, do not appear on the aluminium photograph, through the action of the points at

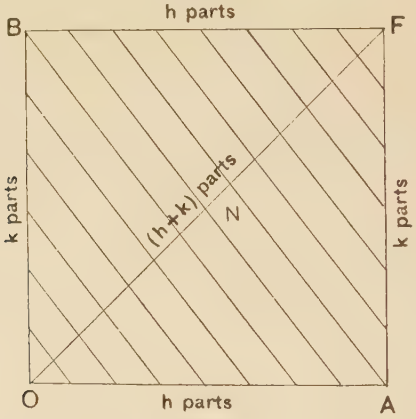


FIG. 93.

the centres of the faces ; and we now proceed to determine the absentees. The set of planes $hx + ky + lz = na$, where n is an integer, divides OA or BF into h equal parts and OB into k equal parts, and therefore OF into $h + k$ equal parts (Figs. 92 and 93). If $h + k$ is even, one plane out of the set passes through N, if it is odd N is exactly half-way between two of the planes. In one case the effects of the points O and N add together, in the other they destroy each other. A similar proposition holds as to the relation between O and L, O and M.

If therefore h, k, l are all even or all odd, in which cases $h + k$, $k + l$, $l + h$, are all even, the points LMN all help the point O : in other words, all the points of the lattice

lie on one or other of the set of planes (hkl), and the reflection is good. But if one of the three is odd and the other two even, or *vice versâ*, then of the three quantities $h+k$, $k+l$, $l+h$, one is even and two are odd. One of the points at the face centres helps O, the other two are in opposition to O: the two pairs mutually interfere and the reflection fails. It is not necessary to consider the other points in the figure, for the point O stands for all cube corners, L for P and other centres of the bc faces, and so on. We must, therefore, strike out a number of the planes in the first column of the table, leaving only those for which hkl are all odd or all even, and the remainder will be those which we should find in a photograph of the cubic close packed arrangement, and which we actually do find in the case of aluminium.

If we refer to the table on p. 147 we see that the largest spacings in the aluminium crystal are, in order of magnitude, those of the (111), (200), (220), (311) and (222) sets of planes. The length of the edge of the cubic cell is 4·043; and the spacings of these planes are—as can be found directly from the figures in the table—2·33, 2·02, 1·43, 1·215, 1·163 respectively. The wave-length of the molybdenum α ray is 0·712 A.U. The corresponding values of θ, the glancing angle are 8° 48′, 10° 9′, 14° 25′, 17° 2′, 17° 49′.

If r is the radius of the ring on the photographic plate we have $r = D \tan 2\theta$ where D is the distance from the crystal C to the plate at P. Substituting the various values of θ in this equation we find that the radii of the five innermost rings are respectively, $0{\cdot}317D$, $0{\cdot}370D$, $0{\cdot}551D$, $0{\cdot}676D$ and $0{\cdot}717D$. The circles in Fig. 97 are drawn in these proportions and may be compared with the rings of Figs. 89, 96, Plate VII.

The lines of γ iron, shown in Fig. 94, Plate VII, are similarly spaced: they are set out in the upper part of Fig. 94*a* on the proper scale for comparison with Westgren's photographs. There are one or two β lines in the photograph which are not shown in the figure.

The α, β and δ phases of iron possess a different structure. If we go back to the single cube, and then consider the effect

of placing a representative point at its centre, we shall find a new ring system, which is characteristic of these phases and of other structures based on the body-centred cube.

The set of planes (h, k, l) which divides OA, OB, OC into h, k, l equal parts respectively divides OG into $h+k+l$ equal parts because OG is the projection of OA, AE and EG. If $h+k+l$ is even, the centre of the cube lies on one plane out of the set, and so all the representative points lie on planes belonging to the set. There is, therefore, a reflection. If $h+k+l$ is odd the centre of the cube and all points like it are half-way between the planes that pass through O and points like O. In this case, therefore, the reflection fails. The more important planes that remain in the table are, therefore,

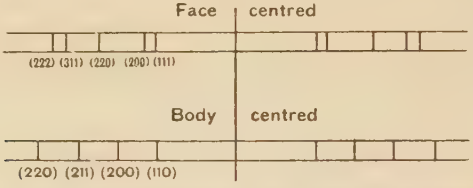


FIG. 94*a*.—The principal lines of iron in its different phases.

110, 200, 211, 220 . . . . This set is shown in lower part of Fig. 94*a* for comparison with the α iron photograph in Fig. 94: the coincidence is obvious. We conclude, therefore, that the structure of α iron is that of the body-centred cube. It is easy to calculate from the measurements of ring diameters that the edge of the cube has the value 2·855, and thence that the cube contains two atoms. As the body centred cube has two representative points, one occupying the corners of the cube and one the centre, each point must represent one atom. The structure of iron can be described by saying that every atom occupies the centre of a cube and has eight neighbours at the corners. The cube is not the unit cell because it contains two atoms which are exactly alike in their relations to their surroundings. The unit cell can only contain one such element of pattern : it may be drawn as in Fig. 11*b*.

The series of photographs obtained by Westgren and Phragmen of iron at various temperatures throws much

light on the long known transformations. Four modifications of iron have been recognised, the first, α, denotes its condition when the temperature is below 800° C. In this range it is magnetic. From 800° to 900° iron is non-magnetic, and is said to be in the β modification. At 900° iron undergoes another change, marked by a sudden slight diminution of volume and an absorption of heat. At 1400° there is again a change. Of these four modifications the photographs show that α, β and δ are built on the model of the body-centred cube, and γ on that of the face-centred. The sudden change of volume in passing from β to γ is readily understood as due to a change in the mode of packing of the atoms, for the cube-centred packing of spheres is not so close as the face centred. We ought not, indeed, to assume that the spheres representing the iron atoms are of the same size in the two systems of packing; in fact, the calculations from the photographs show that they cannot be so, yet the explanation is true in the main.

It is of great interest that the transformation from α to β is not a change of structure, nor indeed any change that can be detected by the X-rays. We do not understand why the two body-centred structures α and δ should be magnetic, while β is not. Magnetism is a consequence of some more subtle condition than any which we have yet been able to detect.

Other metals that possess a similar structure are the alkali metals, lithium, sodium and potassium, vanadium, chromium, molybdenum, tantalum and tungsten.

Many metals are formed on the second system of close packing already referred to. If we begin by putting down spheres on a plane surface so as to form a first layer, the centres of the spheres being represented by the dots of Fig. 95, and upon this a second layer in which the sphere centres are represented by circles, we have so far followed the procedure of the first system of close packing. But now we place the spheres of a third layer so that the centres overlie the centres of the first, a fourth overlying the second, and so on. This arrangement is packed as closely as the other, but it leads to a hexagonal structure. The hexagons

are clearly visible when projected upon the paper as in the figure, but there is no hexagonal projection on any other plane. The crystal has a unique axis, perpendicular to the

FIG. 95.

paper. The circles are not in this case exactly like the dots, because the triangle of dots which is both above and below a circle has its base towards the bottom of the paper and its apex towards the top, while each dot has above and below a triangle of circles which faces the opposite way. A unit

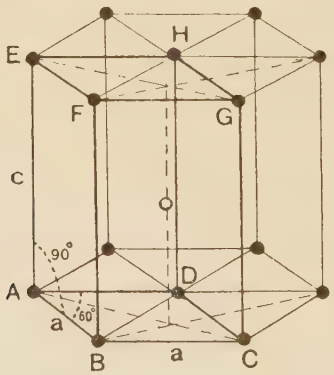


FIG. 95*a*.—The prism outlined heavily and lettered at its corners is the unit cell of a hexagonal close-packed structure.

cell must contain one circle and one dot, or it would not be completely representative : it can be formed by picking out points as in Fig. 95*a*, the one dot being represented by the

eight dots at the eight corners, and the one circle by the circle shown in position inside the named cell. If spheres are packed in this way the ratio $c/a = 1{\cdot}63$. From the table it will

ELEMENTS SHOWING HEXAGONAL CLOSE-PACKING.

Atomic Number.	Element.	a	c/a
4	Be	2·283	1·58
12	Mg	3·22	1·624
22	Ti	2·92	1·59
24	Cr ?	2·714	1·625
27	Co	2·514	1·633
30	Zn	2·657	1·86
40	Zr	3·23	1·59
44	Ru	2·686	1·59
48	Cd	2·960	1·89
58	Ce	3·65	1·62
72	Hf	3·32	1·64
76	Os	2·714	1·59

be seen that only a few of the elements contained in it, though their structures are like that of the figure, follow it so closely that the ratio has exactly the value which it should have if the atoms were spheres. If the distance from the centre of one atom to the next is modified by surroundings, such a divergency need not be unexpected, since the conditions along and across the axis differ from each other.

A perfect ring photograph implies that the crystalline particles are absolutely irregular in their distribution with respect to the incident pencil of X-rays. If any sort of regularity is imposed upon them the rings cannot be complete. This is illustrated by Fig. 96, which is the photograph obtained from a drawn aluminium wire : the rings are still to be seen, but in some parts only faintly. Their intensities are gathered together into spots.

It is clear that the act of drawing a wire must tend to force into the unique direction, viz. that of drawing, some line which in each crystal has a standard relation to the crystal lattice. The photograph may be expected to and does show the extent to which this has taken place. If the effect were

complete, if the rolling had put the standard lines of the various crystals into absolute parallelism, the photograph would then be exactly like the so-called ' rotation ' photograph, as illustrated in Figs. 18 and 25. For, when the minute crystals all have one direction in common, and are otherwise irregularly oriented, we must get the same results as we should in the case of a single perfect crystal rotated about an axis. The existence of both vertical and horizontal symmetry in the pattern shows that the preferred direction is perpendicular to the pencil of X-rays : and this is what we should expect, because the wire was so placed that the direction of drawing was perpendicular to the pencil, and the preferred direction must be that of the drawing. The photograph shows that the orientation of the crystals was not complete, because each circle can still be traced in full, and the spots are somewhat extended along the circles to which they belong. We can imagine every grade of concentration of the spots corresponding with varying degrees of the approach to parallelism. In this case the appearance of the photograph indicates that the effect is not far from being complete.

It is to be expected that the subjection of a material to any kind of treatment, drawing, rolling, stamping, annealing, will produce ' fibre ' of this kind. It may be well to point out that this has nothing to do with the existence of flaws, cavities, inclusions or other large scale irregularities. It relates to a state, or disposition of the minute crystals which the substance contains. So also this peculiar condition is found in living things : it occurs in various parts of plants and animals, in fibres, shells, bones, muscles and so on. Such a disposition greatly affects the properties of the material and is of very frequent occurrence, as the X-rays reveal to us if we did not know it before. Consequently the X-ray photographs showing the presence of fibre are of particular interest and importance. There is in all likelihood a wide application of the X-ray methods to the examination of the consequences when substances animate and inanimate are changed by treatment and growth. It is worth while

therefore, to consider in detail the photograph of Fig. 96 and to find the meaning of each spot and line that it contains. Such a study will show how we can discover from the photograph the direction of the line which in each crystal has been set parallel to the direction of drawing, the extent to which the fibre effect has been completed, and many other facts relating to the condition of the substance.

We therefore proceed to calculate the positions on the aluminium circles (see Fig. 97) at which we should expect to find the spots in a given case. In order to carry out this further calculation it is necessary to assume some particular direction in the crystal cell as that which is set in the direction of the axis of the wire : if the positions of the spots calculated on the assumed direction agree with the photograph a right choice has been made. To save time, we choose at once the correct direction, that of the cube diagonal. Let us consider, therefore, the form of the rotation photograph when a face-centred cube is rotated about the cube diagonal. The spots lie at intersections of the circles with the layer lines. No matter how we place the crystal the radii of the circles remain the same ; but the positions of the layer lines do not. Also, spots lie at some of the intersections, but not at all of them. We, therefore, proceed to find those positions in the particular case we have assumed.

The axis of rotation coincides with the diagonal of the unit cubic cell, and the points O, P, of Fig. 21 may now represent the lattice points at the ends of the diagonal. The hyperbolae are the intersections of the plate with cones of revolution having OP as axis. The semi-vertical angle of any one of the cones is $\cos^{-1} n\lambda/OP$, where n has the values 0, 1, 2, 3, . . . From these data the hyperbolae can be drawn : they are represented by dotted lines in Fig. 97. We have now to identify each spot with its proper point of intersection of layer-line and circle.

We take as origin the point O, Fig. 92, and as axes the three cube edges that meet in O. Let a be the length of an edge.

All spots on the equator are due to planes that pass through both O and P. The (hkl) set of planes divide OP into

$h+k+l$ parts as we have seen already (p. 150). Consequently for all sets that pass through both O and P,

$$h+k+l=0.$$

This condition is satisfied by the planes $(2\bar{2}0)$ and by no other set of planes corresponding to any one of the five circles we have drawn. This determines the position of the $2\bar{2}0$ spot; it is shown in the figure at the intersection of the equator with the (220) circle.

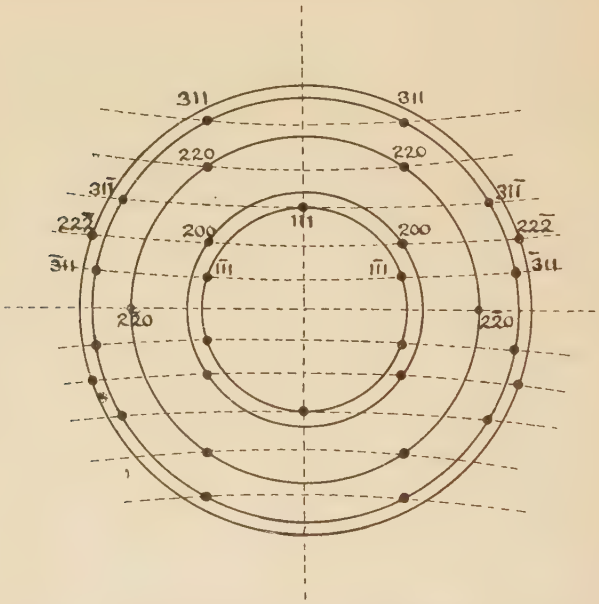


FIG. 97.—Characteristic array of spots due to the rotation of the face-centred cubic structure about the cube diagonal.

Similarly, if a spot is to be found on the first layer line, we have the condition $h+k+l=\pm 1$, which is satisfied by the $(1\bar{1}1)$ and (311) sets of planes. For points on the second hyperbola $h+k+l=\pm 2$. This is satisfied by (222) and (200). On the third hyperbola are (111) and $(31\bar{1})$; on the fourth (220) and on the fifth (311). The spots have been accordingly inserted in the figure, which should now be compared with the photograph of Fig. 96.

The radial streaks in the photograph are due to want of homogenity in the X-ray beam. If we were to calculate the form of the figure for a different wave-length we should find that it had expanded or shrunk as a whole, according as the new wave-length was larger or smaller than the old, and that its proportions would be well retained so long as the wave-length was not made too large. Now the pencil of X-rays employed came from a molybdenum target, which emitted not only α and β rays, but also, the voltage employed being sufficient for the purpose, a wide diffuse band of rays of much shorter wave-length, averaging about 0·4 A.U. The β ray has been largely removed by the use of a zirconium filter which absorbs wave-lengths just less than 0·687, much more than wave-lengths just greater than this value.*

As the wave-length of the β ray of molybdenum is 0·631 A.U., the β ray reflections do not appear in the photograph, with great advantage in clearness. But the filter has let through some of the strong general radiation of still shorter wave-length, and this is the cause of the radial streaks referred to. In fact, the figure contains several displays of the whole X-ray spectrum, one of them, for example, containing effects due to general radiation, as well as the first and second order reflections of the α-rays at the points marked $(11\bar{1})$ and (222).

The fact that the small crystals take up positions with cube diagonals in the direction of drawing is a fact of interest to the metallurgist, since it shows a certain relation existing between an applied stress, and a consequent change in the material, with a parallel alteration in physical properties.

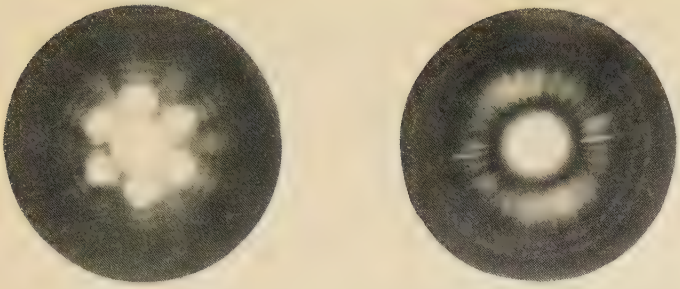
A further example of the X-ray analysis of 'fibre' is shown in Fig. 98, Plate VIII. The two photographs represent the effect of rolling on copper: in Fig. 98(a) the X-rays were perpendicular to the direction of rolling; in Fig. 98(b), they were parallel. The orientation is far from complete, but we can see the (111) and (200) rings, with the approximately hexa-

* The effect is known as 'critical absorption.' A description of it will be found in any treatise on the X-rays.

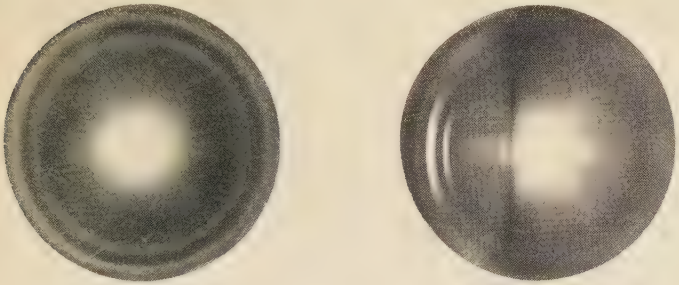
gonal set of ' streaks ' inside them. In this case, also, the cube diagonal has been set in the direction of rolling. The appearance of Fig. 98(*b*) is quite different. Clearly, the state of the copper ought to be the same all round the direction of rolling if there be no influence due to the form of the sheet, and apparently there is no such influence. In other words, all directions at right angles to the direction of rolling should be alike. The homogeneous α rays of the pencil should show their effect in narrow complete circles, and the heterogeneous rays should give rise to complete circles of a diffuse character : the photograph is in agreement with these expectations, except that the individual crystals are not so small as to give the smooth appearance due to a fine powder. There is a certain broken structure in it.

An effect of a different kind is shown in Fig. 99, Plate VIII (*a*) and (*b*). Magnesium has a hexagonal structure, and it appears that, when the metal is rolled, the small crystals of which the material is composed are arranged so that the basal plane of the hexagonal lattice is parallel to the surface of the sheet. Otherwise, there is complete disorder. The arrangement of the crystals resembles that of a pack of cards thrown down upon the table ; the cards are more or less parallel to the table, but otherwise are lying in all positions. In this case a photograph taken with the X-rays perpendicular to the surface of the sheet should show complete circles due to such reflections as can take place. The inclination of the layers to the incident X-rays varies not very widely on each side of a right angle, so that the number of reflections is necessarily limited if the X-rays are homogeneous. When the pencil of X-rays is passed through the crystal in any other direction there is no longer the same uniformity in all directions round the rays, and the circles shrink into arcs, as in Fig. 99(*b*). One half of the photograph shows part of the circle due to the basal plane ; the other is blank, being shielded by the material itself.

The completeness of the rings may be broken in another way. If the fragments are not sufficiently fine, we find, as we might expect, a granular formation, the spots being due



FIGS. 98*a* and 98*b*.—Photographs of rolled copper sheet. Left, X-rays perpendicular to the direction of rolling; right, parallel thereto. (Clark.)



FIGS. 99*a* and 99*b*.—Photographs of magnesium. (Rosenhain.)

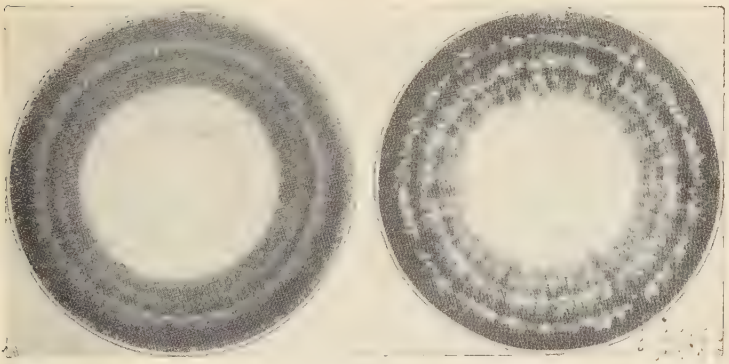


FIG. 100.—Photographs of duralumin (Clark). Left, resistant to intercrystalline corrosion; right, poor specimen, corroded. The difference in quality may be due to the size of the grains, which is greater in the right-hand specimen than in the left.

to separate crystals. An example of this effect is shown in Fig. 100, Plate VIII.

Alloys offer a very wide field for research, and, since they play such an important part in modern metallurgy, the X-rays have been applied by many workers in the hope of solving some very complicated and pressing problems. Considerable progress has been made and knowledge gained in spite of the difficulties of technique and interpretation. Yet it is still to the future and to the skill which experience will bring that we must look for the solutions of many difficulties. Into such an immense subject the work that has already been done has made a relatively small advance. The first question to be asked is, naturally, as to the structure of the alloy. Sometimes, it would seem, the answer is simple. Let us take, for example, the alloys of gold and copper or nickel and palladium, which mix their constituents in any proportion, or, in the language of metallurgy, form an unbroken series of solid solutions. In the case of all these metals the structure is built on the face-centred cube, and this remains unchanged except for a gradual alteration in dimensions between the limiting values of the separate structures of the two constituents.

In the first of these alloys the length of the cube edge changes gradually from 4·073, the value for gold, to 3·610, the value for copper : in the second case from 3·499 (nickel) to 3·950 palladium. It is to be supposed that atoms of one kind gradually replace atoms of the other at various points of the lattice, causing a corresponding shrinking or expansion.

But, of course, a binary alloy cannot show such a uniform change if the two constituents crystallise on different lattices. Thus, for example, a nickel-iron alloy is body-centred when the iron preponderates, the nickel not exceeding 25 per cent. If, however, the iron is less than 70 per cent., the nickel governs the structure and gives it the form of the face-centred cube.

Bronzes and brasses are very complex substances which not only form solid solutions, one in the other, but also compounds, that is to say, crystalline substances containing

the constituents in definite proportions. The difficulties of research are greatly increased by this added intricacy of composition. Nothing could show more clearly than the following Table the complications of the subject, and at the same time the surprising agreement between the results of two groups of investigators who have attempted independently to solve the problems of structure.

TABLE XXIX.—BRASS

	Owen and Preston	Jette, Westgren, and Phragmen
α	0–38 per cent. Zn Solid solution Zn in Cu Face-centred cubic 3·608 to 3·696	0–32 per cent. Zn Solid solution Zn in Cu Face-centred cubic 3·610 to 3·688
β	48·5 per cent. Zn Body-centred cubic $a =$ 2·946	46·9 per cent. Zn Body-centred cubic $a =$ 2·945. Basis CuZn
γ	66·6 per cent. Zn Rhombedral hexagonal $a = 4·136$ $c/a = 0·649$	61·7 to 67·7 Zn Cubic. $d_{(100)} = 8·850$ to 8·887 52 atoms per cube Solution in Cu_4Zn_9
δ	75 per cent. Zn Hexagonal close-packed $a = 2·776$ $c/a = 1·475$	
ϵ	79·5 per cent. Zn Solid solution $a = 2·718$ $c/a = 1·585$	80·3–86·1 per cent. Zn Solid solution $a = 2·75$ $c/a = 1·55$–$1·60$
η	- - - - -	96·5 per cent. Zn $a = 4·916$ axial ratio 1·844
Zn	$a = 2·670$ $c/a = 1·860$	$a = 2·662$ $c/a = 1·856$

The metals and their alloys provide good examples of the many problems to which X-ray analysis can be applied.

They are but a portion of the materials which we use and handle and are interested in. But we see how the analysis can give some information concerning the crystal structure of every known compound ; falling far short indeed in most cases of what we wish to know, but nevertheless new knowledge which only needs time to grow in extent and usefulness. Once known a structure can be studied in connection with all its physical properties, a subject scarcely touched as yet. Some attempts have been made by Born, Madelung and others to connect structure with properties in the case of the simple rocksalt structure, and the refractive index of Iceland spar has been calculated. But many opportunities for similar investigations have not yet been taken in hand, not even, for example, the rotatory power of quartz. The X-rays lead in this direction to a vast field of enquiry.

Even more interesting perhaps than the structure of the single crystal is the composition of a mass of crystals perfect or imperfect. The properties of such a mass depend not only on the nature of the crystals of which it is composed, whether of one sort or of many, but also upon the sizes of the crystals and their orientations. We have seen, in the case of the metals, how all these details can be examined separately and unmistakably, how every compound can, so to speak, be made to write its own signature on the photographic plate or in the curve plotted from the readings of the ionisation spectrometer. In chemical analysis we first destroy any solid structure, bringing the substance to be investigated into solution. But in this case the structure remains intact : that which gives the substance its characteristic as a solid body is the direct subject of investigation by the X-ray methods. The solid is one of the most prominent forms of the earth materials. Liquids and gases have their own importance, but the solid body is, of course, deeply concerned in all the processes which make the history of the world, and in life itself. When we know their various designs we can begin to study those structural forces which hold atoms and molecules together and are only partially in evidence in the liquid and gaseous states.

And so, in concluding these lectures, I return to the thesis which I stated at their commencement. We have not had until now a method of making an organised attack upon the structure of the solid body. Our new power is based upon two facts : the one that the arrangement of the atoms and molecules in a solid tends always to regularity and generally attains it in some degree, the other that the X-rays can detect this regularity and measure it. We can lay bare the structure of the solid and examine it in relation to the properties of the solid phase. Thus a new field of enquiry opens out before us in which we may hope to acquire knowledge of value to all the sciences that are concerned with solid bodies, and to all the activities founded on those sciences. Clearly, the new field is a very wide one.

APPENDIX

The few following drawings are given as additional illustrations of the text :—

I

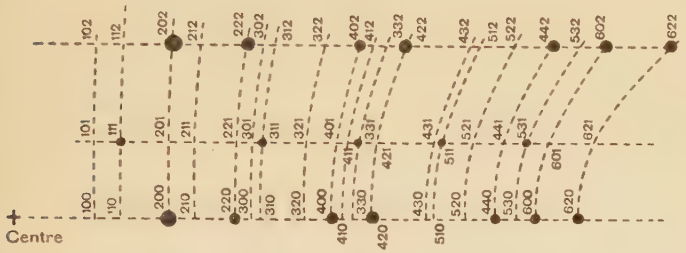


Fig. 101.

Drawing from one quadrant of a rotation photograph of rock-salt, taken on a cylindrical film (p. 37) about a cube edge. If the crystal were 'simple cubic,' spots would appear at every intersection of the horizontal rows and the (more or less) vertical columns (see p. 147). Because the cube is 'face-centred,' spots appear only when $h+k$, $k+l$, $l+h$, are all even. Also, because the sodium and chlorine atoms are placed as in Fig. 32, p. 51, those spots for which h, k, and l are all odd are much weaker than the others. All such spots shown in the figure lie on the first layer. In potassium chloride these also disappear, leaving only spots for which h, k and l are all even. These are again the complete set for a simple cube, but of half the dimensions of the first cube.

II

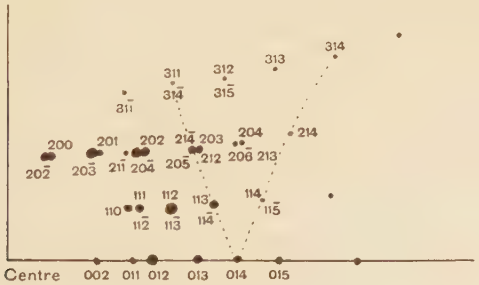


Fig. 102.

Drawing from one quadrant of a rotation photograph of a stilbene crystal ($C_6H_5 . CH_2 . CH_2 . C_6H_5$) about the a axis. The crystal is monoclinic prismatic, four molecules to the cell, and the dimensions are

$$a = 12{\cdot}2 \quad b = 5{\cdot}72 \quad c = 16{\cdot}0 \quad \beta = 113°48'$$

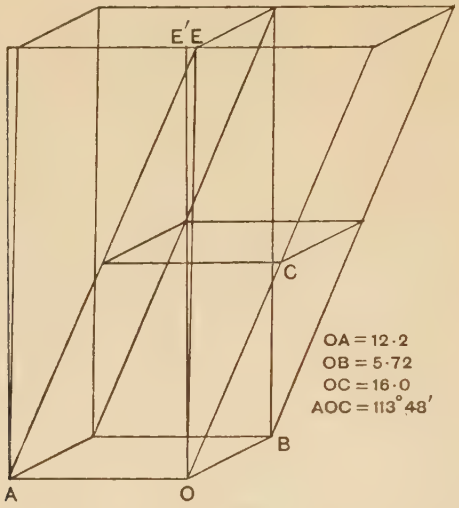


FIG. 103.

These are set out in Fig. 103, which also shows that a cell may be drawn with edges OA, OB, OE, which is nearly orthorhombic. It contains two lattice points and is therefore not a unit cell. On account of the approximation to the orthorhombic form there are many cases in which pairs of planes have nearly the same spacing, so that the corresponding spots overlap, *e.g.* 113 and $11\bar{4}$, 203 and $20\bar{5}$, 311 and 314, and so on. In consequence, the diagram has a certain simplicity which makes it easy to follow lines such as those mentioned on p. 45. Two of these lines are shown, dotted, in the figure. OE' is drawn perpendicular to OA (see p. 45).

III

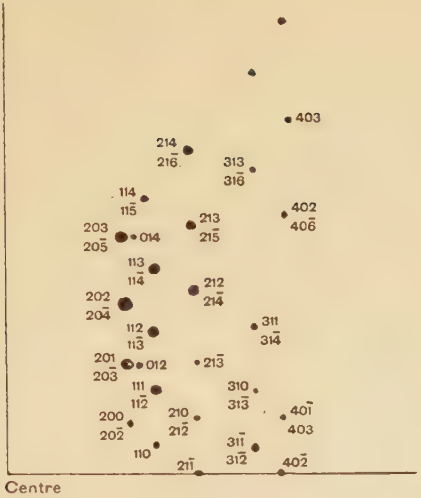


FIG. 104.

Drawing from one quadrant of a rotation photograph of a stilbene crystal about the line OE' in Fig. 103, which is perpendicular to the *ab* face of the crystal. As already explained in the note to Fig. 102, the cell having OA, OB, OE as edges is nearly orthorhombic. Consequently, the spots now lie on lines which are nearly vertical (p. 44). Each vertical column contains the planes due to one zone, the axis of which lies in the *ab* face. The various layer lines are also distinct, though in fact they show, when examined on the full plate of spots, slight irregularities, due to the fact that OE' does not pass (as OE does) through neighbouring lattice points. A set of planes that divides OA into h parts and OC into l parts divides OE into $h+2l$ parts. Thus the nth row contains the spots for which $h+2l = \pm n$.

IV

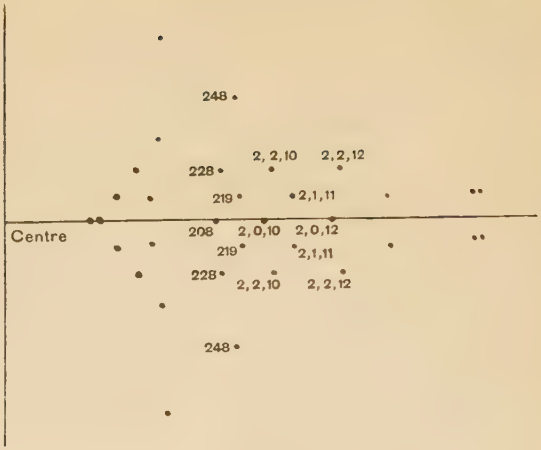


FIG. 105.

Drawing from one half of a rotation photograph of a crystal of naphthalene tetrachloride $C_{10}H_8Cl_4$ about the b axis. The cell for which $a = 7{\cdot}9$, $b = 10{\cdot}3$, $c = 14{\cdot}2$, $\beta = 112° 40'$, contains four molecules, but it is twice the volume of the unit cell. If the corners of the cell are lattice points, so also is the centre of the cell : a somewhat unusual construction. Each molecule has one element of symmetry of its own, so that full monoclinic prismatic symmetry is attained although the unit cell only contains two molecules. The structure is ' body centred.' Consequently, as in the case of a iron, only those planes appear for which $h + k + l =$ an even integer. The photograph therefore shows in some parts a curious diamond-like arrangement : (208), (228), (248) occur, but not (218) nor (238) : so also (219) occurs, but not (209) nor (229). The arrangement of the spots on approximately vertical lines is easily followed.

INDEX

A

Absolute determination of wave lengths, 52.
Alloys, 159.
Aluminium, 156.
Aluminium wire, 153.
Anthracene, 108.
Association of molecules, 111.
Atomic radii, 114.

B

Benzil, 124.
Bernal, J., 63.
Beryllium oxide, 116.
Black spot, 131.
Born, M., 161.
Bragg, W. Lawrence, 116-118, 122.
Bragg's law, 11-16.
Brass, 160.
Brown, G. B., 117.

C

Calcite, 52, 78.
Calcium fluoride, 66.
Cell element, 89.
Cell, unit, 89.
Cellulose, 140.
Compton, A. H., 10.
Copper, fibre in rolled, 157.
Corundum, 116.
Crysoberyl, 122.
Cubic close packing, 144.
Cubic lattice, 24.
Cubic planes, 23.
Cubic spacings, 147.

D

Debye, P., 143.
Diamond, 56.
Diamond model, 60.
Diffraction principle, 2.
Digonal symmetry, 93.
Dispersion in X-ray spectrum, 35.
Disthene, 118.

E

Enhancement principle, 120, 135-139.
Equator line, 40.
Etch figures of sylvine, 54.

F

Fatty acids, 125.
Fibre structure, 154.
Fluorspar, 66.

G

Gibbs, R. E., 123.
Graphite, 63.
Graphite, lubricating qualities, 64.

H

Hexagonal close packing, 152.
Hull, A. W., 143.
Hydrocarbons, 126.

I

Ionic crystals, 56.
Ionisation spectrometer, 31, 57.
Iron, 149-151.
Iron pyrites, 70-77.

K

Ketones, 132.

L

Lattice, 8.
Lattice, cubic, 23, 24.
Laue, M. von, 1, 27.
Laue method, model, 28.
Layer lines, 42.
Light and X-rays, 4.
Lubricating qualities of graphite, 64.

M

Magnesium, 158.
Magnetite, 116.
Madelung, E., 161.
Molecule in the crystal, 53.

Molybdenum target, 34.
Monticellite, 122.
Müller, A., 1, 127, 135, 137.

N.
Naphthalene, 108.
Naphthalene tetrachloride, 108.
Nomenclature, 21.

O
Octodecane, 131.
Olivine, 122.

P
Phragmen, G., 150.
Powder method, 45.
Powder photograph of aluminium, 143.
Pyrites, 70-77.

Q
Quartz, 79-87.
Quartz, α, 84.
Quartz, β, 82, 83.
Quartz, twinning of, 85-86.

R
Radii of atoms, 114.
Reflection, Bragg's law, 11-16.
Rhodium target, 32.
Rocksalt, 46, 50.
Rocksalt photographs, 47.
Rotation photographs, 37.
Rotation photograph of cubic crystal, 48, 156.
Rotation photograph of Al wire, 153.
Rubber, 140-142.
Ruby, 116.

S
Sapphire, 116.
Scherrer, P., 143.
Shift, crystallographic, 94.
Siegbahn, 52.
Silicates, 115-123.
Shearer, G., 132.
Space groups, 89, 100-101.
Spectrometer, 31.
Stearic acid, 126.
Stilbene, 163.
Structure factor, 18.
Surface action, 6.
Sylvine, 49.

T
Trigonal symmetry, 98.
Trigonal symmetry of iron pyrites, 71.
Twinning of quartz, 85-86.

U
Unit cell, 8, 89.
Unit of pattern, 7.

W
Wave length of X-rays, 9.
West, 116, 118, 122.
Westgren, A., 149, 150.
Wire, aluminium, 156.

X
X-rays, nature of, 1.
X-rays, wave length, 9.

Z
Zincblende, 68.

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